

NOAA STATUS AND TRENDS

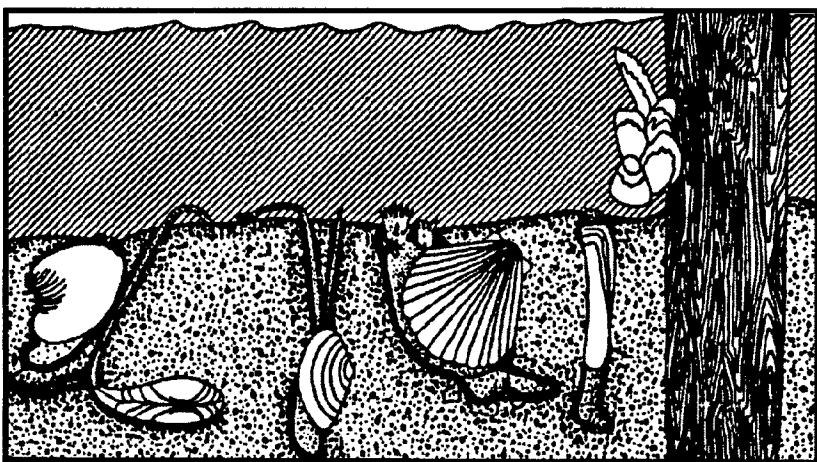
Mussel Watch Project

Technical Report

Year IX

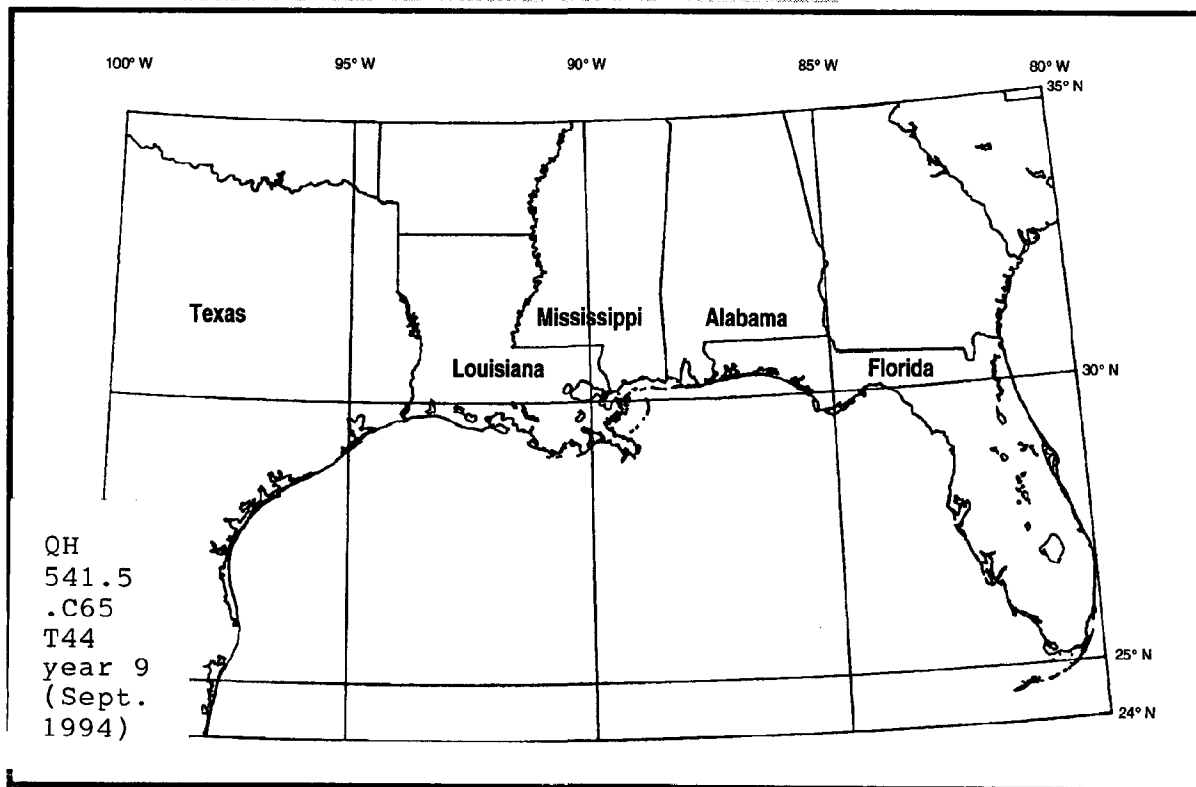


The Geochemical and
Environmental Research Group
Texas A&M Research Foundation



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Mussel Watch Project

Year 9 Technical Report

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NOAA'S NATIONAL STATUS AND TRENDS (NS&T) MUSSEL WATCH PROGRAM — GULF OF MEXICO

The purpose of the NOAA National Status and Trends (NS&T) Mussel Watch Project is to determine the long-term temporal and spatial trends of selected environmental contaminant concentrations in bays and estuaries. The key questions in this regard are:

- (1) What is the current condition of the nation's coastal zone?
- (2) Are these conditions getting better or worse?

This report represents the Year 9 Technical Report from this multi-year project. These questions have been addressed in detail as evidenced by the scientific papers and reports that have resulted from the Geochemical and Environmental Research Group's (GERG) interpretations of the Gulf Coast data (Table 1). Publications not included in GERG's previous Technical Reports are contained in this technical report.

This report is an update on the current condition of the Gulf of Mexico coastal zone, based on results from Years 1 through 9 of the NOAA NS&T Mussel Watch Project. Following is a brief sampling survey of these years:

- Year 1 - 49 sites (147 stations) of the original 51 sites were successfully sampled. Sediments and oysters were analyzed at triplicate stations from all sites.
- Year 2 - 48 sites (144 stations) of the original 51 sites were successfully sampled. Sediments and oysters were analyzed at triplicate stations from all sites.
- Year 3 - Twenty (20) sites were added to the original list of 51 sites for a total of 71 sites. Sixty-four (64) sites (192 stations) of the 71 sites were sampled (only 19 of the new sites were sampled). Oysters were analyzed at triplicate stations from all sites. Sediments were analyzed at only the new sites (three stations analyzed per site).
- Year 4 - Seven (7) new sites were added (only six of the new sites were successfully sampled). Sixty-seven (67) sites (201 stations) of the 78 total sites were sampled. Oysters were analyzed at triplicate stations from all sites. Sediments were analyzed at only the new sites (three stations analyzed per site).
- Year 5 - Three (3) new sites were added to the sampling project (only two of these sites were successfully sampled; 79:MBDR and 80:PBSP). Sixty-eight (68) sites (204 stations) of the 80 total sites were sampled. Oysters were analyzed at triplicate stations from all sites.

Sediments were analyzed at only the new sites (three stations analyzed per site).

- Year 6 - Two (2) new sites were added to the sampling project (81:BHKF in Bahia Honda Key, FL and 63:LPGO in Lake Pontchartrain, LA). Sixty-four (64) sites (192 stations) were sampled. Oysters were analyzed at triplicate stations from all sites. Sediments were analyzed at only the new sites (three stations analyzed per site).
- Year 7 - Five new sites were established including three new sites in Puerto Rico (Sites 86 to 88) and two new sites in Choctawhatchee Bay (Sites 84 and 85). Sixty-seven (67) sites were analyzed. Only one oyster analysis was conducted at each of the old sites on a composite from the three stations. Sediments were analyzed at the five new sites and one site in Florida (PBPH) (three stations analyzed per site).
- Year 8 - Sixty-eight (68) existing sites were sampled. Only one oyster analysis was conducted at each of the existing sites on a composite from the three stations. Sediments were not collected at any sites.
- Year 9 - A total of 55 sites were visited and 51 of them were successfully sampled. Four of the originally scheduled sites were devoid of any live oysters. Two new sites were established in Florida Bay (Flamingo Bay, FBFO; and Joe Bay, FBJB). At these is these new sites both triplicate sediments and oysters were sampled. No other sediment samples were taken this year. Only one oyster analysis was conducted at each of the existing sites on a composite from the three stations.

Details of the sample collection and location of field sampling sites are contained in a separate report titled "Field Sampling and Logistics in Year 9".

The oyster and sediment samples were analyzed for contaminant concentrations [trace metals, polynuclear aromatic hydrocarbons (PAH), pesticides and polychlorinated biphenyls (PCBs)], and other parameters that aid in the interpretation of contaminant distributions (grain size, oyster size, lipid content, etc.). The analytical procedures used and the QA/QC Project Plan are detailed in a separate report titled "Analytical Methods". The data that were produced from the sample analyses for Year 9 are found in a separate report titled "Analytical Data".

A complete and comprehensive interpretation of the data from the National Status and Trends Project for oyster data coupled with the sediment data is an on-going process. We have begun and are continuing that process as evidenced by this report and the scientific manuscripts that we have published or submitted for publication (Table 1). As part of the data interpretation and dissemination, over 40

presentations of the NOAA NS&T Gulf Coast Mussel Watch Project were given at national and international meetings. With eight years of data, the question of temporal trends of contaminant concentrations has been addressed. A general conclusion found for most contaminants measured is that the concentrations have remained relatively constant over the nine year sampling period. This general trend, however, is not observed at all sites. Some sites show significant changes (both increases and decreases) among the years. Continued sampling is addressing the frequency and rates of these changes.

Exceptions to this general trend are found for DDTs and TBT. When historical data for DDT in bivalves is compared to current NS&T data, a decrease in concentration is apparent. Also based on TBT data collected as part of the NOAA NS&T Mussel Watch Project, a decline in TBT concentration in oysters is apparent. Both declines may be in response to regulatory actions.

During Year 3 of this project, 20 new sites were added. These sites were chosen to be closer to urban areas, and therefore, to the sources of contaminant inputs. These new sites were not, however, located near any known point sources of contaminant input. These sites were added to better represent the current status of contaminant concentrations in the Gulf of Mexico. Over the subsequent years of the project (Years 4 through 9) additional sites have been added to increase the representative coverage of the Gulf of Mexico and U.S. Caribbean territories.

While sampling sites for this project were specifically chosen to avoid known point sources of contamination, the detection of coprostanol in sediment from all sites indicates that the products of man's activities have reached all of the sites sampled. However, when compared to known point sources of contamination, all of the contaminant concentrations reported are, in most cases, many orders of magnitude lower than obviously contaminated areas. The lower concentrations in Gulf of Mexico samples most likely reflect the fact that the sites are further removed from point sources of inputs, a condition which is harder to achieve in East and West Coast estuaries. In fact, new sites added in Years 3 through 7 are closer to urban areas and generally had higher contaminant concentrations. An important conclusion derived from the extensive NS&T data set is that contamination levels in Gulf Coast near shore areas remain the same or are getting better, and most areas removed from point sources are not severely contaminated.

This document represents one of three report products as part of Year 9 of the NS&T Gulf of Mexico projects. The other two reports are entitled:

- Analytical Data, Year 9
- Field Sampling and Logistics, Year 9

Table 1. GERG/NOAA NS&T PUBLICATIONS

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Reprint 1

**Accumulation and Depuration of Organic
Contaminants by the American Oyster
(*Crassostrea virginica*)**

**Jose L. Sericano, Terry L. Wade and James M.
Brooks**

**ACCUMULATION AND DEPURATION OF ORGANIC CONTAMINANTS
BY THE AMERICAN OYSTER (*CRASSOSTREA VIRGINICA*)**

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ABSTRACT

Oysters and other bivalves are widely used to assess the levels of environmental contamination; however, very little actual field calibration of bivalves has been done. The purpose of this research, therefore, has been to evaluate the uptake and depuration of selected PCBs and PAHs in transplanted American oysters, *Crassostrea virginica*, under field conditions in Galveston Bay, Texas. Transplanted oyster were found to bioaccumulate contaminants and reach concentrations nearly equal to those of indigenous oysters for PAHs and low molecular weight PCBs within 30 to 48 days. In contrast, high molecular weight PCBs did not reach equivalent concentrations. When returned to a clean environment, oysters significantly depurated PAHs and low molecular weight PCBs. There were, however, differences in depuration rates when newly contaminated oysters were compared to chronically contaminated oysters. Oysters are useful tools in biomonitoring studies but have their limitations. Transplant studies help to establish these limitations on the use of oysters as sentinel organisms to avoid misleading interpretation of the oyster contaminant concentrations.

INTRODUCTION

Contamination of the coastal marine environment by a number of organic compounds of synthetic or natural origin has received increasing attention over the last several years. Biomonitoring of these compounds in the aquatic environment has been well established and bivalves are generally preferred for this purpose. The rationale for the "Mussel Watch" approach using different bivalves, e.g. mussel, oysters and/or clams, has been summarized by different authors (Goldberg *et al.*, 1978; Farrington *et al.*, 1980; Phillips, 1980; Risebrough *et al.*, 1983) and its concept has been applied to several monitoring programs during the last decade (Farrington *et al.*, 1983; Martin, 1985; Tavares *et al.*, 1988; Wade *et al.*, 1988; Sericano *et al.*, 1990; Tripp *et al.*, 1992).

Several studies have examined the dynamics of the uptake and depuration of trace organic contaminants; however, the information found in the literature is confusing. As an example, Table 1 lists a number of studies published over the last two decades that report the depuration of different hydrocarbon mixtures by bivalves. The contradicting results of these studies, most of them carried out in laboratories, are obvious. Bivalves need to be "calibrated" under real environmental conditions to be valuable as bioindicators of organic contamination. Uptake and depuration rates of organic contaminants, compound selectivity, interaction between different xenobiotics, seasonal effects on the body concentrations of xenobiotics and differences between species need to be known to take full advantage of the "Mussel Watch" concept.

The present study was designed to examine the rate of uptake and depuration of selected trace organic contaminants, e.g. polynuclear aromatic hydrocarbons (PAHs) and polychlorinated biphenyls (PCBs), in oysters (*Crassostrea virginica*) during transplantation experiments in two locations in Galveston Bay, Texas. Uptake and depuration rates of selected organic compounds by transplanted oysters were determined. Clearance rates

determined for newly contaminated oysters are compared to depuration rates found in chronically polluted oysters.

MATERIALS AND METHODS

Experimental design

Approximately 250 oysters of similar dimensions were collected from a relatively uncontaminated area in Galveston Bay, Hanna Reef, and transplanted in 24x70 cm net bags, containing 25-30 individuals per bag, to a new location near the Houston Ship Channel in the upper part of the Bay (Fig. 1). Composite samples of 20 transplanted and 15 indigenous oysters were collected at 0, 3, 7, 17, 30, and 48 days during the first phase of the transplantation experiment. The remaining Hanna Reef oysters were then back-transplanted to their original location in Galveston Bay. At the same time, approximately 150 indigenous oysters from the Ship Channel site were also transplanted to the Hanna Reef area. Composite samples of 20 oysters from each population were collected at 0, 3, 6, 18, 30, and 50 days after transplantation.

Analytical method

The analytical procedures used during this study are modifications of previously reported methods (MacLeod *et al.*, 1985) and are fully described elsewhere (Wade *et al.* 1988; Sericano *et al.*, 1990). Briefly, approximately 10-15 g of wet tissue are dried with Na_2SO_4 and macerated with methylene chloride with a Tisumizer for 3 minutes after the addition of internal standards. This extraction is repeated twice more with new additions of methylene chloride. Combined extracts are concentrated to a final volume of 2 mL in hexane for silica gel-alumina chromatography clean-up. Silica gel is activated prior to use by heating at 170°C for 12 hr and then partially deactivated with 5% water. Alumina is activated at 400°C for 4 hr and then partially deactivated with 1% water. The column is slurry-packed in methylene chloride with 10 g of alumina over 20 g of silica gel. Sample

extracts are eluted from the column using 50 mL of pentane (f_1 =aliphatic hydrocarbons) and then with 200 mL of a pentane:methylene chloride (50:50) mixture (f_2 =chlorinated hydrocarbons, including PCBs, and PAHs). The f_2 -fraction is further purified by high performance liquid chromatography (Krahn *et al.*, 1988).

The PAHs in f_2 -fraction were separated and quantitated by GC/MS using an HP-5880-GC interface with an HP5970-MSD. Sample extractss were injected in the splitless mode on a 30 m x 0.25 mm (0.32 μ m film thickness) DB-5 fused silica capillary column at an initial temperature of 60°C. The oven temperature was programmed at 12°C min⁻¹ to 300°C and held at the final temperature for 6 min. The mass spectral data were acquired using selected ions for each of the PAHs. The instuments were calibrated using a five-point calibration curve and the calibration was checked by running continuing calibrations standards with each set of samples with no more than 6 hr between calibrations checks. Analyte concentrations were calculated using the mean relative response factors for each analyte relative to the internal standards added before extraction.

Samples were analyzed for PCB congeners by fused-silica capillary column GC-ECD (Ni⁶³) using a Hewlett-Packard 5880A GC in the splitless mode. The DB-5 capillary column (30 m x 0.25 mm; 0.25 μ m film thickness) was temperature-programmed from 100°C to 140°C at 5°C min⁻¹, from 140°C to 250°C at 1.5°C min⁻¹, and from 250°C to 300°C at 10°C min⁻¹ with 1 min hold time at the beginning of the program and before each program rate change. The final temperature was held for 5 min. Injector and detector temperatures were set at 275°C and 325°C, respectively. These compounds were quantitated against a set of authentic standards that were injected at four different concentrations to calibrate the instrument and to compensate for non-linear response of the detector.

Quality control/quality assurance (QA/QC)

Interim reference materials as well as spiked blanks, duplicate samples and spiked samples were analyzed along with each sample set as part of the laboratory

QA/QC program. Evaluation of the analytical methods and possible sources of error are a continuing and ongoing process in order to assure the reliability of the data.

RESULTS AND DISCUSSION

The concentrations of some of the organic contaminants increased dramatically during the seven-week exposure period. Comparatively, concentrations of some individual PAHs and PCBs in indigenous oysters during the first phase of this experiment were fairly constant. The analyte concentrations in native oysters represent the time-integrated contaminant concentrations available to the oysters in solution, adsorbed onto particles and incorporated with food.

Polynuclear Aromatic Hydrocarbons

Initial concentrations of total PAHs, ie. sum of 24 individual analytes (Sericano *et al.*, 1993), in transplanted oysters increased from 290 ng g⁻¹ to a final value of 4360 ng g⁻¹. By the end of 48 days, transplanted oysters accumulated these PAHs to levels that were not statistically differentiable from the concentrations measured in native individuals (Fig. 2). Two- and three-ring PAHs were detected in low concentrations in both transplanted and indigenous oysters while four- and five-ring compounds were detected in high concentrations. The PAHs accumulated to the highest concentrations by transplanted oysters were: pyrene>fluoranthene>chrysene>benzo(e)pyrene>benzo(b)anthracene. Although in slightly different order, approximately the same PAHs were reported to be preferentially accumulated by clams and mussels exposed to sediments contaminated with relatively high PAH concentrations, i.e. pyrene>benzo(e)pyrene>benzo(b)fluoranthene>

benz(a)anthracene (Obana *et al.*, 1983) and chrysene>benzo(b)fluoranthene>fluoranthene>benzo(e)pyrene>benz(a)anthracene (Pruell *et al.*, 1986), respectively.

Hanna Reef and Ship Channel oysters showed statistically significant depuration ($p<0.05$) of four- and five-ring PAHs after relocation to the Hanna Reef area. Depurations of these aromatic compounds by both groups of oysters were approximately exponential. This is indicated in Fig. 3 where the concentration of selected PAHs plotted on a semi-log plot approximate straight lines.

Kinetics parameters describing uptake and release of PAHs can be calculated assuming the first-order equation

$$dC_t/dt = k_u C_w - k_d C_t \quad (1)$$

where C_t is the PAH concentration in the transplanted oyster at time= t , C_w is the PAH concentration in the seawater, and k_u and k_d are the uptake and depuration rate constant, respectively. If the C_w at Hanna Reef is regarded as zero, i.e. $C_w=0$, which is considerably reasonable because of the very low PAH concentrations measured in indigenous oysters, then equation (1) reduces to

$$dC_t/dt = -k_d C_t \quad (2)$$

or, after integration,

$$\log C_t = \log C_0 - (k_d/2.301) t \quad (3)$$

where C_0 is the PAH concentration in oysters at the time of their relocation to the Hanna Reef area. Using this equation and the PAH concentrations corresponding to both oyster populations during the depuration period, values of k_d can be calculated.

Statistical analyses, at the $\alpha = 0.05$ level, of the regression lines of the logarithm of the concentrations versus sampling time for the depuration period showed significant

differences between the slopes, i.e. depuration rates, measured for Hanna Reef and Ship Channel oysters were significantly different. The biological half-life, $t_{1/2}$, can be derived from equation (3)

$$t_{1/2} = 0.693/k_d \quad (4)$$

The half-lives are reported in Table 2. They ranged from 9 and 10 days for pyrene to 26 and 32 days for fluoranthene in Hanna Reef and Ship Channel oysters, respectively. Most of the values were, however, between 10 and 16 days. These findings are in agreement with those of Pruell *et al.* (1986) who reported half-lives between 14 and 30 days for selected PAHs in mussels (*Mytilus edulis*) exposed in the laboratory to environmentally contaminated sediments. Contrasting with other reports (Table 1), both studies suggest that bivalves are able to depurate the accumulated hydrocarbons in fairly short periods of time.

The difference in depuration rates between both newly and chronically contaminated oysters is evident at the end of the 50-day depuration period when the concentrations of PAHs grouped by number of rings or individually are compared (Fig. 4). At the end of the depuration period, the total PAH concentration in chronically contaminated oysters were about 40% higher than the final concentration measured in originally uncontaminated oysters. Total PAH concentrations decreased from 4,400 to 360 ng g⁻¹ and from 4,400 to 500 ng g⁻¹, respectively. This observation is in agreement with an earlier work by Jackim and Wilson (1977) who reported that the depuration rates of N° 2 fuel oil compounds observed in chronically exposed bivalves (*Mya arenaria*) were considerably lower than those observed in organisms after an acute exposure.

Polychlorinated Biphenyls

PCB concentrations in transplanted oysters increased from 30 ng g⁻¹ to 850 ng g⁻¹ after the 48-day exposure period. Pentachlorobiphenyls were the compounds accumulated to the highest concentrations in transplanted and native oysters (Fig. 5). In comparison,

practically no octa-, nona- or decachlorobiphenyls were detected in either oyster group. Contrasting with PAHs, not all the PCB homologs measured in transplanted oysters reached the concentration encountered in indigenous individuals by the end of the first phase of this experiment. While there were no statistically significant differences in the tri- and tetrachlorobiphenyl concentrations measured in transplanted and native oysters, significant differences were observed in the total concentrations of penta- and hexachlorobiphenyls. It seems evident that a longer exposure period is needed for the higher molecular weight PCB, i.e. congener 110, to reach an steady state concentration (Fig. 6).

Hanna Reef and Ship Channel oysters showed statistically significant depuration ($p < 0.05$) of low molecular weight PCBs when relocated to the Hanna Reef area. Originally uncontaminated oysters depurated PCBs at a faster rate than chronically contaminated oysters. The clearance rates of high molecular weight PCBs were significantly slower in both oyster populations. This differential PCB depuration can be observed in Fig. 7 where the concentrations of selected PCBs at the end of the uptake and depuration periods are shown.

Biological half-lives (BHL) for selected PCB congeners in Hanna Reef and Ship Channel oysters ranged from 22 to 130 days and from 22 days to >year, respectively (Table 2). These BHL compare well with those observed in previously reported studies using bivalves. Pruell *et al.* (1986) reported half-lives for some tri-, tetra-, penta- and hexachlorobiphenyls in mussels exposed to resuspended contaminated sediments ranging from 16.3 to 45.6 days. Similar to the present study, the biological half-lives of PCBs increased with the number of chlorine atoms in the biphenyl rings. Langston (1978) also reported that the less chlorinated PCB congeners were depurated more rapidly by bivalves (*Cerastoderma edule* and *Macoma balthica*) with half-lives from 5 to 21 days for selected di-, tri- and tetrachlorobiphenyls. In contrast, the concentrations of hexachlorobiphenyls, and some of the pentachlorobiphenyls, did not decrease during the 21-day study. Courtney

and Denton (1976) reported that environmentally contaminated clams and clams exposed to Aroclor 1254 in the laboratory did not depurate PCBs during three months in control seawater.

From this study, it is clear that oysters will react differently to sudden increases in environmental concentrations of PAHs or PCBs as a consequence of, for example, accidental spills. While PAHs and low molecular weight PCB concentrations seem to reach a steady-state within about a month, high molecular weight PCB congeners might require a much longer period of time, i.e. over 6 months to reach steady-state concentrations. Similarly, the period of time needed for oysters to depurate the accumulated organic contaminants after the spill to accurately represent the actual contamination of a site will be different for PAHs and lower chlorinated PCB congeners compared to higher molecular weight PCBs.

As a general conclusion oysters can be useful tools in biomonitoring studies but results differ for different trace organic contaminants. Transplant studies place boundary conditions on the use of oysters as sentinel organisms. These experimental results can be used to better understand the PCB and PAH data in oyster samples collected from coastal U.S. areas during programs such as NOAA's National Status and Trends (NS&T) "Mussel Watch" Program.

ACKNOWLEDGEMENTS

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Table 1. Results of different hydrocarbon uptake/depuration studies with bivalves reported in the literature.

Bivalve	Exposure	Observation	Reference
Oysters	Nº 2 Fuel Oil (60 days)	Little depuration after 180 days	Blumer <i>et al.</i> (1970)
Oysters	Nº 2 Fuel Oil (49 days)	Nearly complete depuration in 28 days	Stageman and Teal (1973)
Clams	Chronically polluted	Slight depuration after 120 days	Boehm and Quinn (1977)
Oysters	Chronically polluted	Nearly complete depuration with BHL=4.4 days	Wormell (1979)
Oysters	PAHs (15 days)	Analytes below detection limits after 4 days	Pittinger <i>et al.</i> (1985)
Mussels	PAHs (40 days)	Depuration with BHL between 14-30 days	Pruell and Quinn (1986)
Clams	PAHs (2 days)	No depuration in 45 days	Tanacredi and Cardenas (1991)

Table 2. Biological half-lives of selected PAHs and PCBs in transplanted and indigenous oysters.

Analyte	Oysters		Mussels ¹
	Hanna Reef	Ship Channel	
PAHs			
Phenanthrene	-	-	-
Fluoranthene	26	32	30
Pyrene	10	12	-
Benzo(a)anthracene	13	15	18
Chrysene	12	16	14
Benzo(e)pyrene	12	16	14
Benzo(a)pyrene	9	10	15
Indeno[1,2,3-c,d]pyrene	10	11	16
PCBs			
26	22	22	-
28	-	-	16
52	27	45	-
101	55	116	28
110	45	103	-
118	73	299	-
128	76	229	37
149	130	>year	-
153	51	102	46

¹ Pruell *et al.*, 1986

Figure Captions

- Figure 1- Galveston Bay transplantation sites.
- Figure 2- Total and selected individual polynuclear aromatic hydrocarbon concentrations (ng g^{-1} , dry weight) in Hanna Reef and Ship Channel oysters at the end of the 48-day uptake period. Error bars represent one standard deviation from the mean ($n = 4$).
- Figure 3- Selected polynuclear aromatic hydrocarbon concentrations (ng g^{-1} , dry weight) in Hanna Reef and Ship Channel oysters during the uptake and depuration phases of the study. Error bars represent one standard deviation from the mean ($n = 4$).
- Figure 4- Total and selected individual polynuclear aromatic hydrocarbon concentrations (ng g^{-1} , dry weight) in Hanna Reef and Ship Channel oysters at the end of the 50-day depuration period. Error bars represent one standard deviation from the mean ($n = 4$).
- Figure 5- Total polychlorinated biphenyl, grouped by level of chlorination, and selected individual congener concentrations (ng g^{-1} , dry weight) in Hanna Reef and Ship Channel oysters at the end of the 48-day uptake period. Number in parentheses indicates level of chlorination. Error bars represent one standard deviation from the mean ($n = 4$).
- Figure 6- Selected polychlorinated biphenyl concentrations (ng g^{-1} , dry weight) in Hanna Reef and Ship Channel oysters during the uptake and depuration phases of the study. Error bars represent one standard deviation from the mean ($n = 4$).
- Figure 7- Total polychlorinated biphenyl, grouped by level of chlorination, and selected individual congener concentrations (ng g^{-1} , dry weight) in Hanna Reef and Ship Channel oysters at the end of the 50-day depuration period. Number in parentheses indicates level of chlorination. Error bars represent one standard deviation from the mean ($n = 4$).

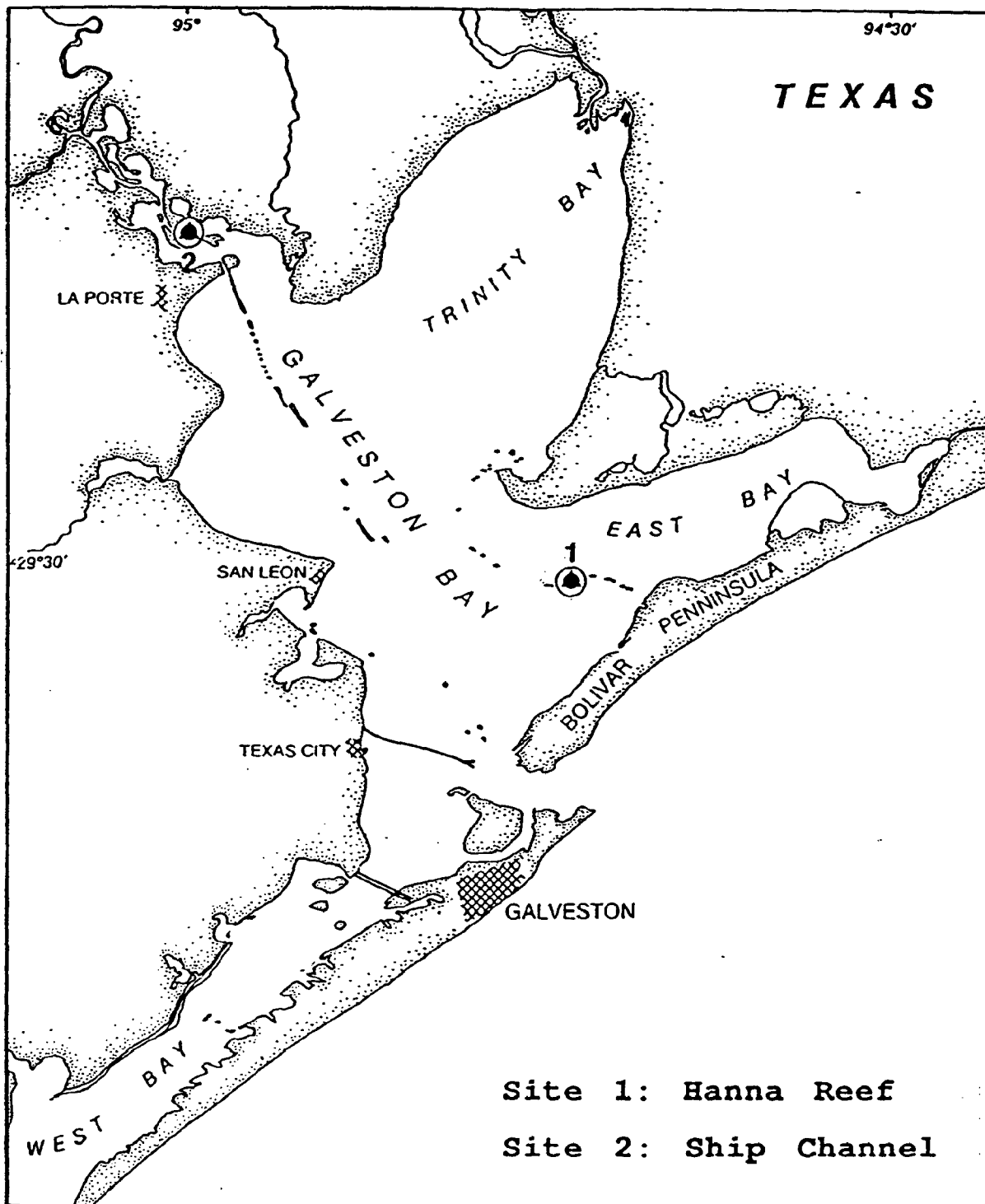


Fig. 1.

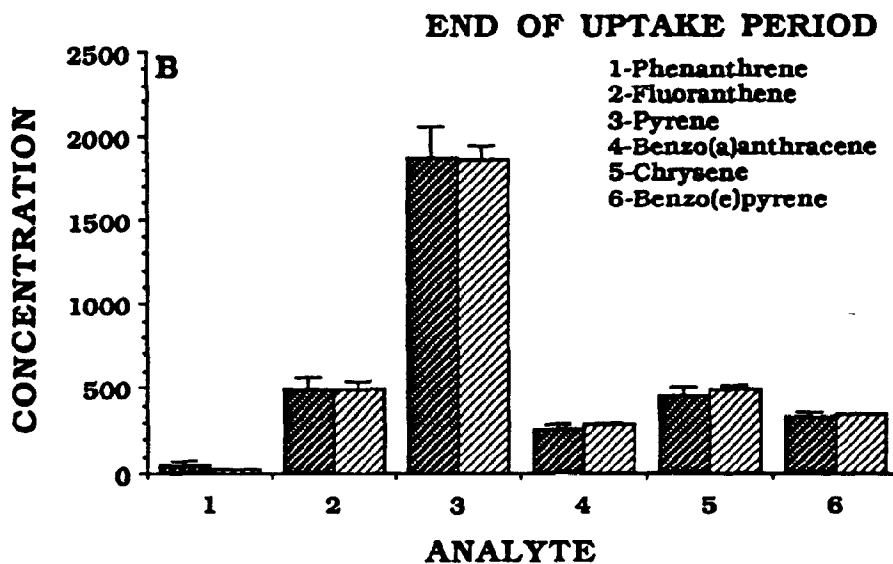
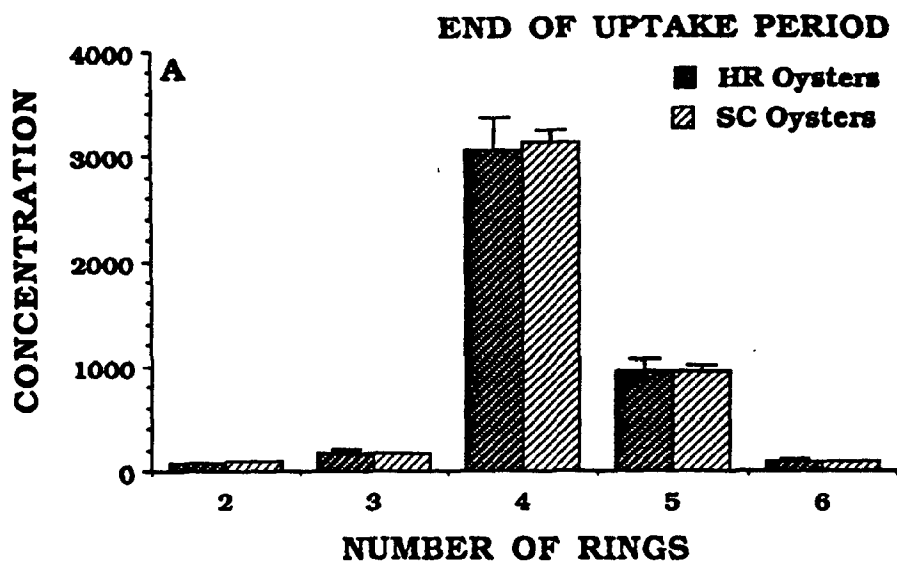


Fig. 2

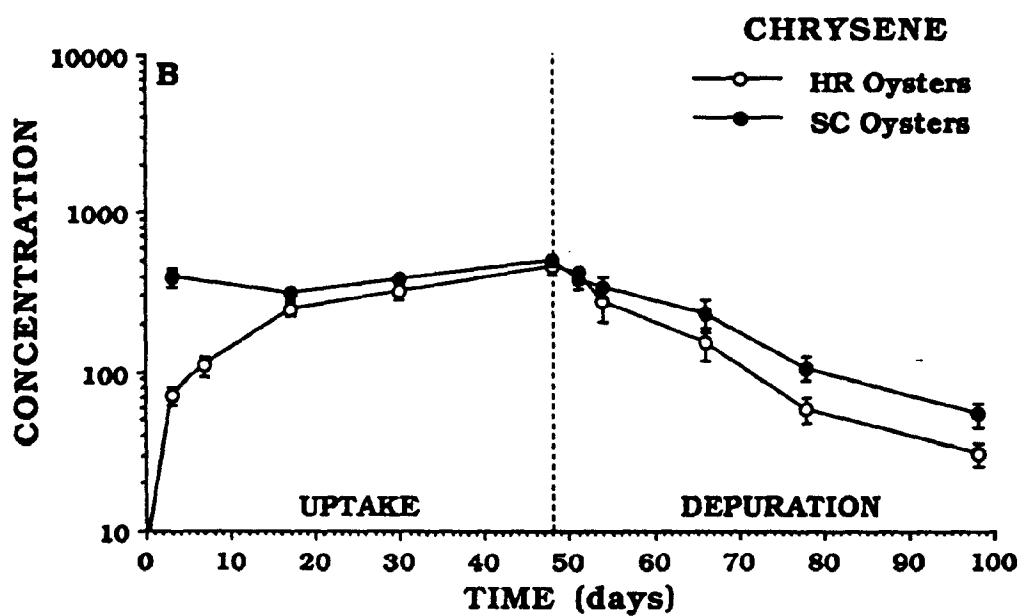
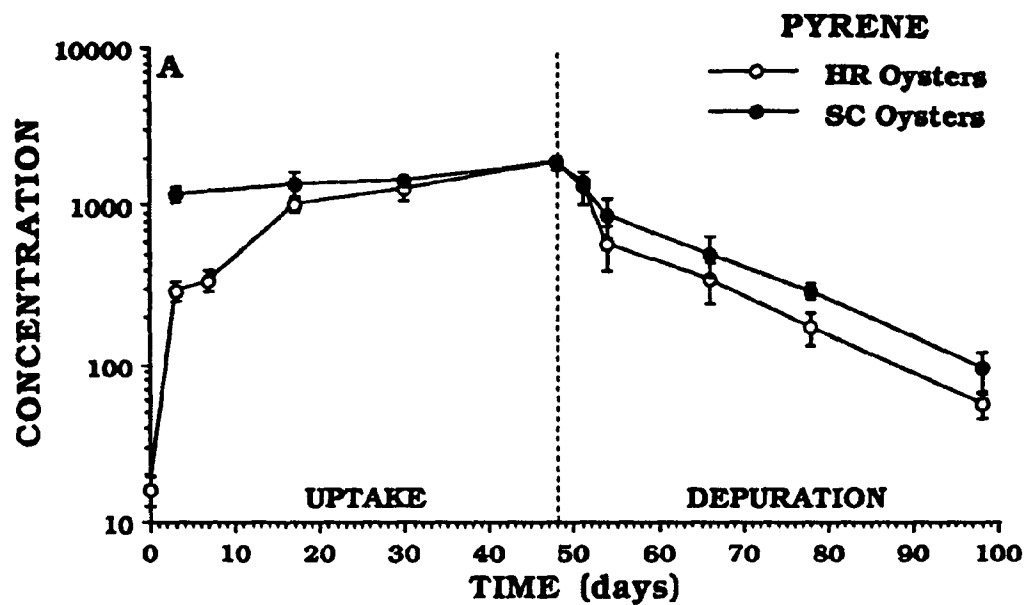


Fig. 3

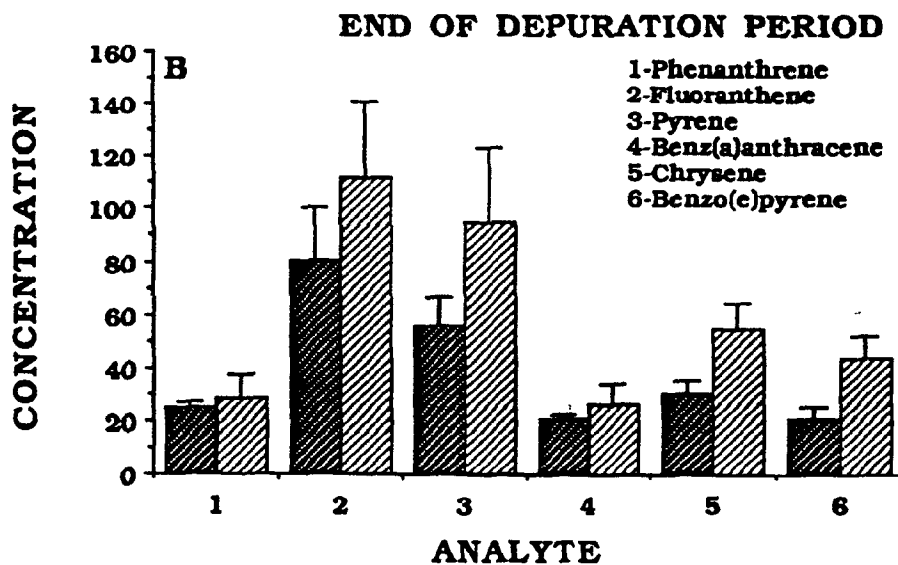
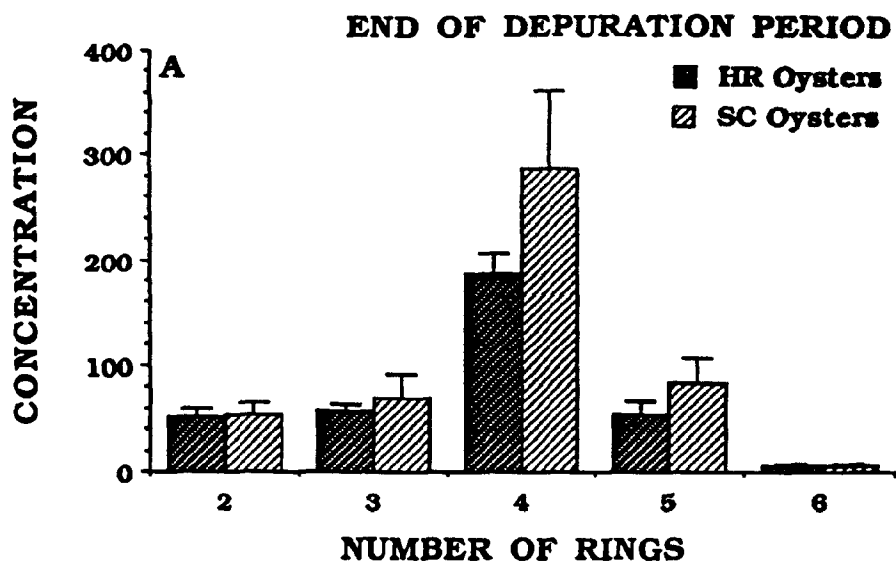


Fig. 4

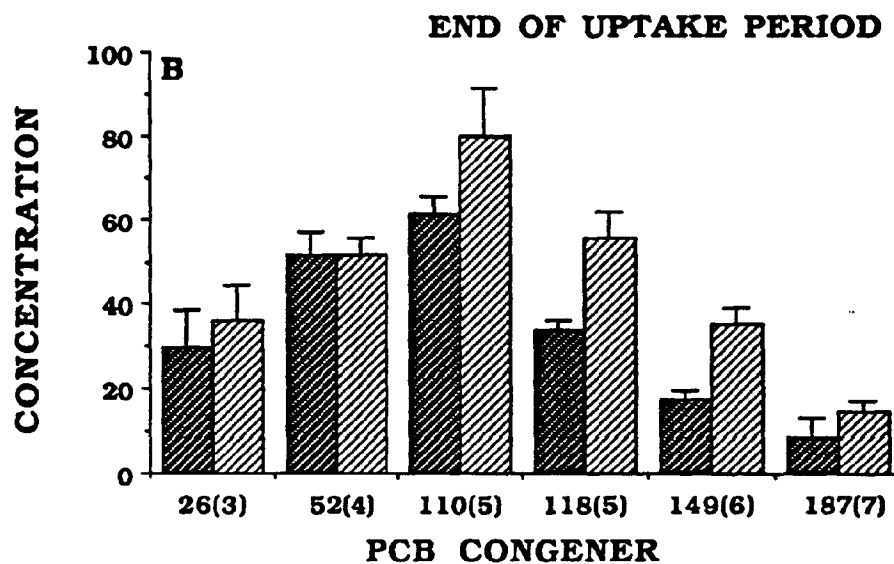
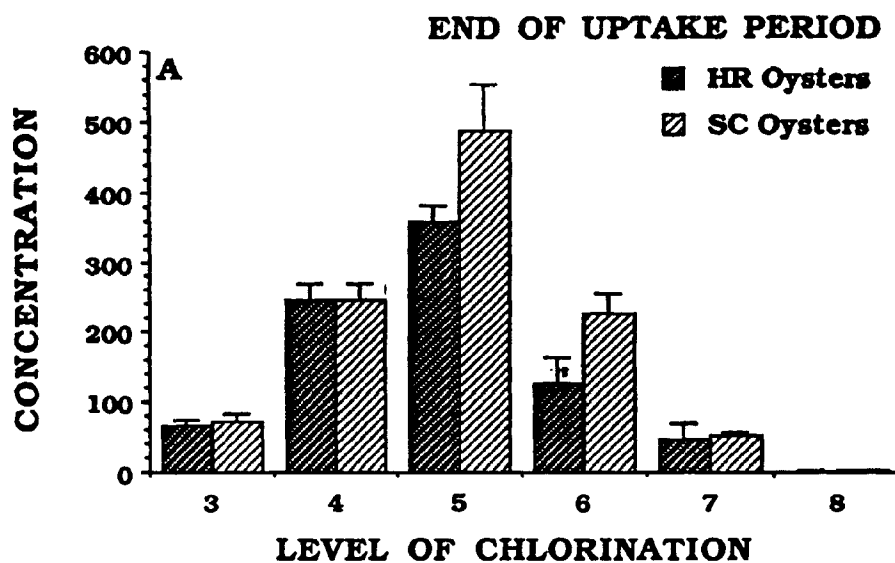


Fig. 5

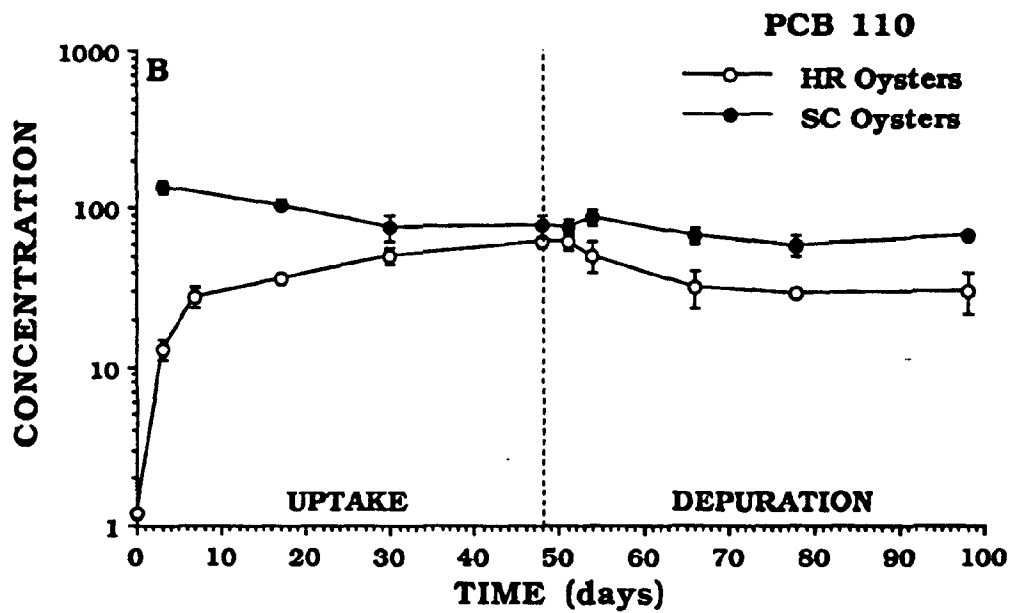
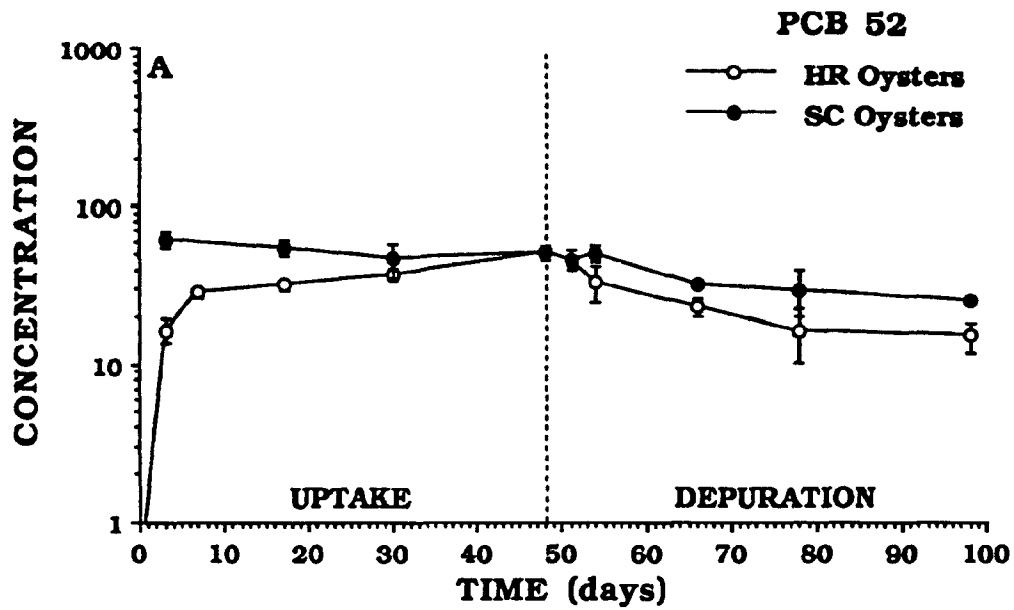


Fig. 6

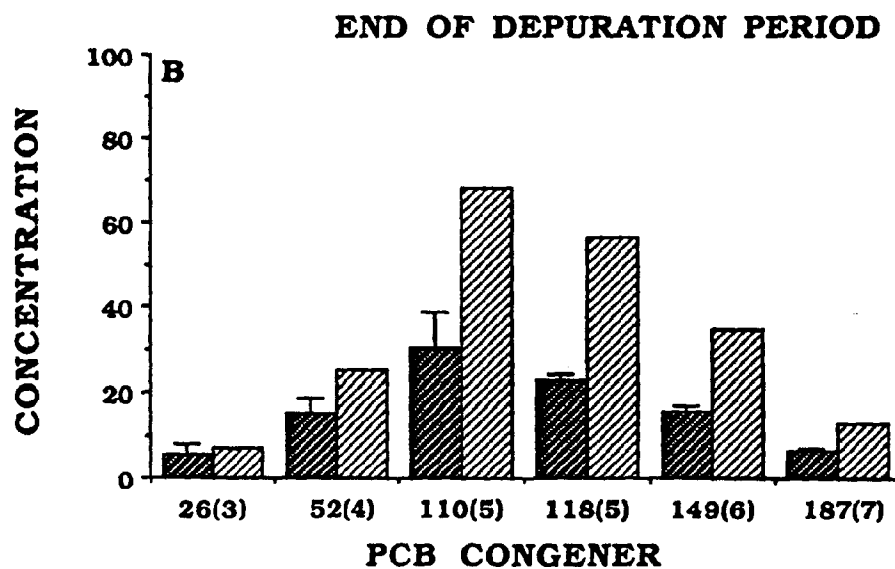
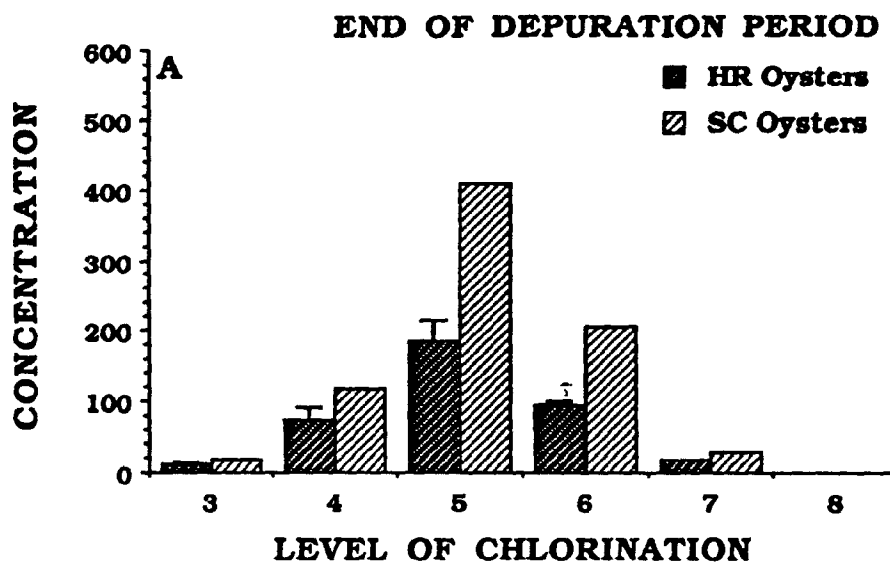


Fig. 7

Reprint 2

**Toxicological Significance of Non-, Mono-
and Di-ortho-Substituted Polychlorinated
Biphenyls in Oysters from Galveston and
Tampa Bay**

**Jose L. Sericano, Stephen H. Safe, Terry L.
Wade and Jame M. Brooks**



TOXICOLOGICAL SIGNIFICANCE OF NON-, MONO- AND DI-ortho-SUBSTITUTED POLYCHLORINATED BIPHENYLS IN OYSTERS FROM GALVESTON AND TAMPA BAYS

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Abstract—Concentrations on non-ortho (77, 126, and 169), mono-ortho (105 and 118) and di-ortho (128 and 138)-substituted PCB congeners were measured in oysters from Galveston and Tampa bays, and reported toxic equivalent factors were used to assess their toxicity. Most of the relative toxicity encountered in the oysters analyzed during this study was due to the presence of planar non-ortho-PCBs (53.8–94.3%), particularly congener 126. In contrast, the contribution of di-ortho-substituted PCB congeners to the total relative toxicity of the samples is negligible (<1%). On average, the contribution of each of these non-, mono-, and di-ortho-substituted PCB congeners to the total toxicity encountered in oysters from Galveston and Tampa bays were $126 > 118 \geq 169 \geq 105 > 77 \gg 138 > 128$ and $126 > 118 > 169 \geq 77 > 105 \gg 138 > 128$, respectively. Based on the reported lower clearance rates of non-ortho- and mono-ortho-substituted PCB congeners compared to other congeners within the same chlorination level, contaminated oysters that are depurated in clean environments will lower their total PCB concentrations, but their original toxicity may not be proportionally reduced.

Keywords—PCBs Toxicity Depuration Oysters Gulf of Mexico

INTRODUCTION

The general concern about the occurrence of PCBs in different environmental compartments is associated with their potential adverse environmental and human health effects. The toxicity of individual PCB congeners is structure-dependent [1–3], and the most toxic PCB congeners—i.e., the planar 3,3',4,4'-tetrachlorobiphenyl (77), 3,3',4,4',5-pentachlorobiphenyl (126), and 3,3',4,4',5,5'-hexachlorobiphenyl (169)—are approximate isostereomers and potent mimics of 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (TCDD). TCDD and related compounds elicit a diverse spectrum of toxic and biochemical responses including body weight loss, dermal disorders, liver damage, thymic atrophy, reproductive toxicity and immunotoxicity, and the induction of CYP1A1 and CYP1A2 gene expression [1–4]. Although epidemiological studies on human and animal populations have not revealed clear evidences of the carcinogenicity of PCBs under environmental exposure, PCBs are strong promoters of hepatic carcinogenesis in laboratory rodents [5].

In recent years there has been considerable interest in studying the occurrence of not only planar PCB congeners but also their mono- and di-ortho derivatives [6–10]. The objective of this study was to determine the toxicological significance of three highly toxic planar PCB congeners (i.e., PCBs 77, 126, and 169) encountered in oyster samples from Galveston and Tampa bays compared to the relatively less

toxic but far more abundant mono- (PCB 105 and 118) and di-ortho (PCB 128 and 138) congeners.

MATERIALS AND METHODS

Sampling

These samples were collected from 3 stations at 12 pre-selected sites in Galveston and Tampa bays (Fig. 1) during the 6-year sampling activities of the National Oceanic and Atmospheric Administration's (NOAA's) National Status and Trends "Mussel Watch" Program (December 1990–January 1991). Distances between stations within each site varied from 100 to 1,000 m. Depending on water depth, oysters (20 per station) were collected by hand, tongs, or dredge, pooled in precombusted jars, and frozen until analysis. More details regarding site locations and sample collections for this program are given elsewhere [11].

Extraction and initial sample fractionation

The analytical procedure used for the extraction, initial fractionation, and cleanup of oyster tissue samples for the analysis of polychlorinated biphenyls (PCBs), including planar PCB congeners, is based on a method developed by MacLeod et al. [12] with a few modifications. Details of this method and its modifications have been fully described elsewhere [13] and only the important steps will be given here.

Approximately 15 g of wet tissue are extracted, after the addition of anhydrous Na_2SO_4 , with methylene chloride using a homogenizer (Tekmar Tissumizer). A small subsample is removed from the total volume for lipid determination. Each set of 8 to 10 samples is accompanied by a complete

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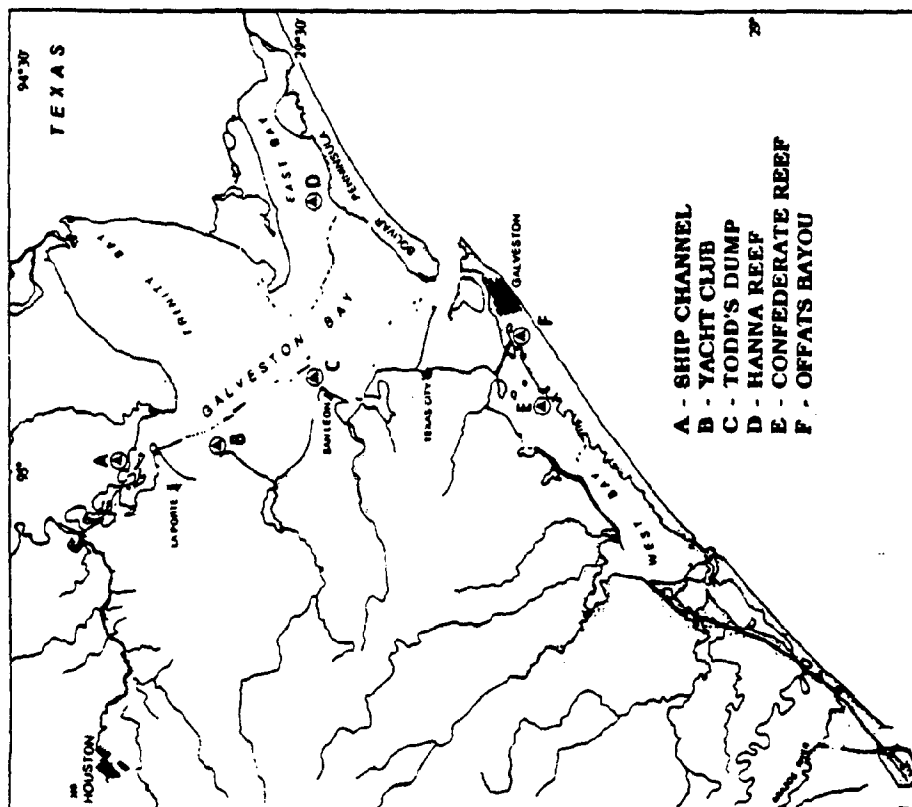
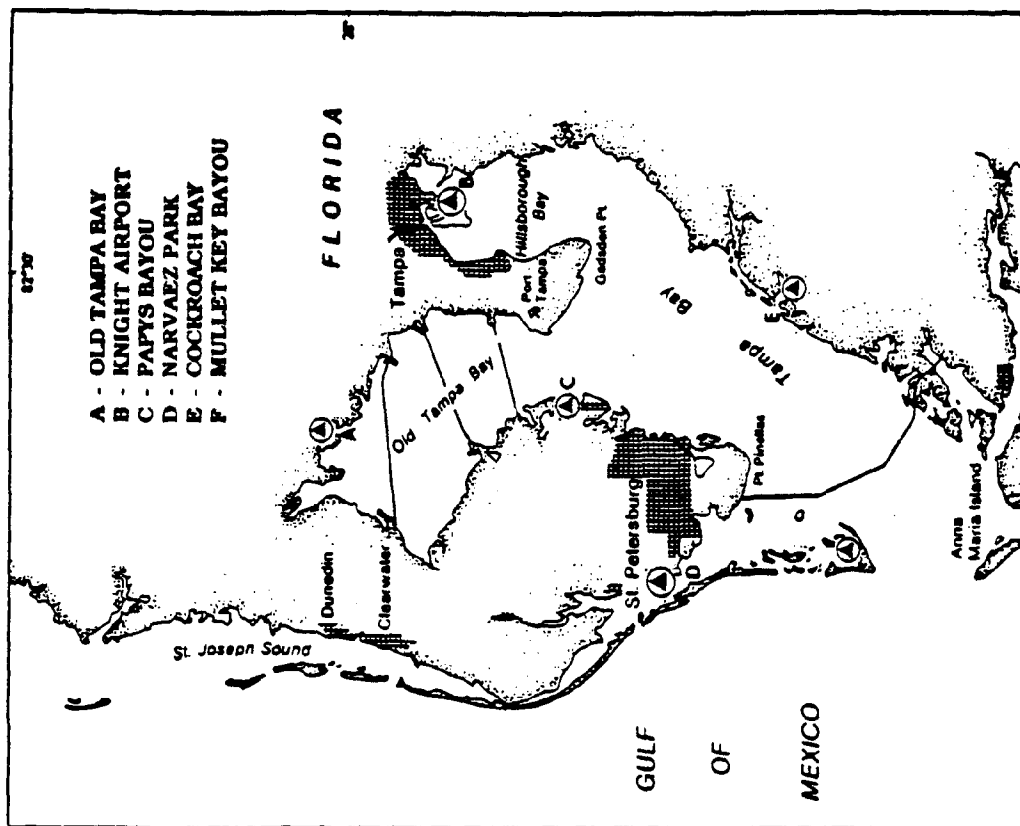


Fig. 1. NOAA's National Status and Trends sampling locations in Galveston and Tampa bays.

system blank and spiked blank or reference material carried through the entire analytical method as part of the laboratory quality assurance/quality control (QA/QC) procedure. Before extraction 4,4'-dibromooctafluorobiphenyl (DBOBF), PCB 103, and PCB 198 are added to all samples, blanks, and reference material as internal standards. Tissue extracts are initially fractionated by partially deactivated silica: alumina column chromatography. The sample extracts are eluted from the column using pentane (f1 = aliphatic hydrocarbons) and pentane:methylene chloride (1:1) (f2 = chlorinated hydrocarbons and PAHs). The second fractions are further purified by high-performance liquid chromatography to remove lipids [14]. Finally, sample extracts are concentrated to a volume of 1 ml, in hexane, for gas chromatographic (GC) analysis.

Isolation of planar PCB congeners

The extraction, initial fractionation, and cleanup of planar PCBs were performed simultaneously with the bulk of the ortho-substituted PCBs. After the final extract concentration to 1 ml, a 0.25-ml fraction was withdrawn for the analysis of planar PCB congeners. Because of the low environmental concentrations expected for planar PCBs, the extracts of oysters collected at the same site were combined as one sample. Thus, the concentrations of planar PCB congeners represent the analyses of composite samples. Before proceeding to the next step, PCB 81 was added to the extracts as internal standard for planar PCB congeners.

The methodology used to isolate planar PCBs in tissue samples has been published elsewhere [15]. Briefly, glass chromatographic columns (10 mm i.d.) are packed in methylene chloride. Two grams of a 1:20 mixture of activated AX-21 charcoal (Super-A activated carbon) and LPS-2 silica gel (low-pressure silica gel, particle size 37–53 μm , 450 $\text{m}^2 \cdot \text{g}^{-1}$), are packed between two layers of anhydrous sodium sulfate. Oyster tissue extracts are sequentially eluted from the column with 50 ml of 1:4 methylene chloride and cyclohexane, 30 ml of 9:1 methylene chloride and toluene, and 40 ml of toluene. The first two solvent mixtures are collected as one fraction (f1) and contain the ortho-substituted PCB congeners. The second fraction (f2), containing the non-ortho-substituted PCB congeners with four, five and six chlorines in meta and para positions, is concentrated to a final volume of 0.05 ml, in hexane, for gas chromatography-electron-capture detection (GC-ECD) analysis.

Instrumental analysis

The PCBs, both planar and nonplanar congeners, were analyzed by fused-silica capillary column, 30 m long \times 0.25 mm i.d. with 0.25 μm DB-5 film thickness, GC-ECD (^{63}Ni) using a Hewlett Packard 5880A GC in the splitless mode.

For the analysis of ortho-substituted PCB congeners, the oven temperature was programmed from 100 to 140°C at 5°C min^{-1} , from 140 to 250°C at 1.5°C min^{-1} , and from 250 to 300°C at 10°C min^{-1} with 1-min hold time at the beginning of the run and at each program rate change. A hold time of 5 min was used at the final temperature. Total run time was 94 min. For the analysis of planar PCB congeners

the oven temperature was programmed from 100 to 150°C at 10°C min^{-1} and from 150 to 270°C at 6°C min^{-1} with 1-min hold time at the beginning of the program and before the program rate change. A hold time of 3 min was used at the final temperature. Total run time was 30 min.

In both analyses, injector and detector temperatures were set at 275 and 325°C, respectively. Helium was used as the carrier gas at a flow velocity of 30.0 cm sec^{-1} at 100°C. A mixture of argon/methane (95:5) was used as the makeup gas at a flow rate of 20 ml min^{-1} . The volume injected was 2 μl .

The PCB congeners were quantitated against a set of standards injected at four different known concentrations to calibrate the instrument and to compensate for the nonlinear response of the electron-capture detector. Tetrachloro-*m*-xylene (TCMX) was used as the GC internal standard to estimate the recoveries of the internal standards. The detection limits for individual planar and nonplanar PCB congeners—estimated on the basis of 2.5 g (dry weight) oyster tissue sample sizes, 1 ml final extract volume, and 2 μl of the extract injected into the GC-ECD—are 0.25 ng g^{-1} and 0.05 ng g^{-1} , dry weight, respectively.

RESULTS AND DISCUSSION

Concentrations of individual planar PCB congeners, as well as concentrations of related mono- and di-ortho-substituted congeners and total PCBs, in oyster samples from 12 sites in Galveston and Tampa bays are shown in Table 1. These concentrations have been corrected by the recoveries of the internal standards—i.e., PCB 103 for ortho-substituted congeners and PCB 81 for planar congeners. In general, recoveries of the internal standards ranged from 65 to 92%.

The highest concentrations of planar PCBs in samples from Galveston Bay were found in oysters collected in the area where the Houston Ship Channel enters into Galveston Bay and the concentrations decreased seaward. High planar PCB levels were also encountered in samples from a site near the city of Galveston. In general, the levels of planar PCBs in Galveston Bay were clearly highest near population centers. The same correlation was observed in Tampa Bay, where the highest planar PCB concentrations were observed in samples collected near the city of Tampa.

The concentrations of congener 77 in different commercial PCB mixtures are 1 to 2 orders of magnitude higher than the concentrations of congener 126 and 3 to 5 orders of magnitude higher than the concentrations of congener 169 [16–20]. Comparatively, average concentrations of congener 77 encountered in oyster samples from Galveston and Tampa bays were 1.5 to 2 times higher than the concentrations of PCB 169 but comparable to the concentrations of congener 126. These results suggest that congeners 126 and 169 are enriched in oyster samples from Galveston and Tampa bays. Selective enrichment of congener 126 and 169 with respect to congener 77 is also apparent in mussels and oyster samples analyzed by different researchers (Table 2). This selective enrichment might be a consequence of the increasing log K_{ow} (logarithm of the octanol/water partition coefficient) with the number of chlorines substituted in the biphenyl rings (6.36, 6.89, and 7.42 for congeners 77, 126, and 169, respectively; Hawker and Connell [21]). In addition, the more highly

Table 1. Non-, mono-, and di-ortho-substituted PCB and total PCB concentrations (ng g^{-1} dry weight \pm 1 SD) in oysters (*Crassostrea virginica*) from Galveston and Tampa bays

Sample	PCB congeners						Total PCB concentrations ^a	Total TEQs ^b	Total TEQs ^c	
	Non-ortho			Mono-ortho		Di-ortho				
	77	126	169	105	118	128				138
Galveston Bay										
Ship Channel	2.0 (20)	2.2 (220)	0.79 (40)	39 ± 4.1 (39)	48 ± 5.8 (48)	4.4 ± 0.6 (0.1)	50 ± 6.7 (1.0)	1,100 ± 120	280	370
Yacht Club	0.33 (3.3)	0.21 (21)	0.19 (9.5)	4.1 ± 1.7 (4.1)	9.0 ± 0.3 (9.0)	1.5 ± 0.2 (<0.1)	13 ± 3.2 (0.3)	210 ± 14	34	47
Todd's Dump	0.14 (1.4)	0.12 (12)	0.05 (2.7)	1.3 ± 0.2 (1.3)	5.2 ± 1.0 (5.2)	0.6 ± 0.2 (0.1)	5.7 ± 1.1 (0.1)	110 ± 18	16	23
Hanna Reef	0.09 (0.9)	0.11 (11)	0.09 (4.5)	0.6 ± 0.5 (0.6)	1.2 ± 0.3 (1.2)	0.6 ± 0.2 (<0.1)	4.3 ± 0.8 (0.1)	50 ± 7.0	16	18
Confederate Reef	0.10 (1.0)	0.09 (9.4)	0.05 (2.6)	0.7 ± 0.6 (0.7)	2.8 ± 0.2 (2.8)	0.7 ± 0.3 (<0.1)	5.0 ± 1.4 (0.1)	77 ± 9.6	13	17
Offats Bayou	0.50 (5.0)	0.40 (40)	0.09 (4.7)	3.2 ± 1.8 (3.2)	10 ± 2.7 (10)	1.0 ± 0.3 (<0.1)	8.7 ± 3.4 (0.2)	160 ± 44	50	63
Tampa Bay										
Old Tampa Bay	0.17 (1.7)	0.32 (32)	0.28 (14)	0.4 ± 0.2 (0.4)	2.4 ± 1.6 (2.4)	0.2 ± 0.2 (<0.1)	4.0 ± 0.8 (0.1)	55 ± 8.5	48	51
Knight Airport	1.5 (15)	0.33 (33)	0.08 (4.2)	7.6 ± 3.7 (7.6)	36 ± 15 (37)	2.0 ± 1.0 (<0.1)	30 ± 13 (0.6)	580 ± 230	52	97
Papys Bayou	0.09 (0.9)	0.10 (10)	0.05 (2.6)	0.4 ± 0.1 (0.4)	3.0 ± 0.7 (3.0)	0.3 ± 0.2 (<0.1)	6.1 ± 2.6 (0.1)	75 ± 27	14	17
Narvaez Park	0.26 (2.6)	0.14 (14)	0.15 (7.5)	1.3 ± 0.2 (1.3)	7.3 ± 1.8 (7.3)	0.6 ± 0.2 (<0.1)	8.9 ± 3.1 (0.2)	120 ± 31	24	33
Cockroach Bay	0.20 (2.0)	0.29 (29)	0.10 (5.0)	0.4 ± 0.2 (0.4)	3.0 ± 1.1 (3.0)	0.2 ± 0.2 (<0.1)	2.8 ± 1.2 (0.1)	49 ± 20	36	40
Muller Key Bayou	ND (-)	ND (-)	ND (-)	0.3 ± 0.2 (0.3)	1.6 ± 0.3 (1.6)	0.2 ± 0.1 (<0.1)	3.3 ± 2.0 (0.1)	38 ± 14	-	2.0

Total 2,3,7,8-TCDD equivalents (TEQs) are expressed in pg g^{-1} dry weight. Individual 2,3,7,8-TCDD equivalents are given in parentheses. ND, none detected.

^aEqual to the sum of all the measurable individual congeners.

^bTotal TCDD equivalents corresponding to the non-ortho-substituted PCB congeners.

^cTotal TCDD equivalents corresponding to the sum of congeners 77, 126, 169, 105, 118, 128, and 138.

chlorinated 126 and 169 isomers are more resistant to metabolic and chemical breakdown compared to the lower chlorinated PCB 77 [1]. On average, the sum of these three highly toxic congeners ranged from 0.26 to 0.62% and from 0.31

to 1.40% of the total PCB load in Galveston and Tampa bays, respectively.

As expected from the small contributions of planar congeners to the total commercial PCB mixtures [16-20], these

Table 2. Concentrations of selected non- and mono-ortho-substituted PCB congeners in bivalves reported in the literature

Species	Location	PCB congeners (pg/g dry wt.)					Reference no.
		Non-ortho			Mono-ortho		
		77	126	169	105	118	
Mussels ^a	Hong Kong	590 (88)	<33 (<5.0)	<4.7 (<0.7)			[7]
Mussels ^a	Hong Kong	4,700 (700)	330 (49)	45 (6.8)			[7]
Mussels	Long Island	400			3,300	8,000	[24]
Mussels ^a	Eastern Scheldt	430 (64)	87 (13)	12 (1.8)	2,900 (430)	10,000 (1,500)	[10]
Oysters ^a	Eastern Scheldt	200 (30)	40 (6.0)	7.3 (1.1)	1,900 (280)	4,500 (680)	[10]
Oysters	Galveston Bay	530	520	211	8,200	13,000	This study
Oysters	Tampa Bay	370	200	110	1,700	8,900	This study

^aReported concentrations were recalculated on dry-weight basis using 15% dry weight. Original concentrations are indicated in parentheses.

congeners were detected at much lower concentrations than some mono- and di-ortho-substituted PCB congeners — e.g., 105, 118, 128, and 138. Individually, the concentrations of these mono- and di-ortho congeners in oyster samples from Galveston and Tampa bays were 1 to 2 orders of magnitude higher than planar PCB concentrations (Table 1).

TCDD equivalents

In a review, Safe [3] discussed the environmental and mechanistic considerations behind the development of the toxic equivalent factor (TEF) concept. Safe proposed provisional TEF values of 0.01, 0.10, and 0.05 for planar PCB congeners 77, 126, and 169, respectively. Similarly, Safe proposed provisional TEF values of 0.001 and 0.00002 for mono- and di-ortho-chlorine-substituted PCB congeners, respectively. Recently, the validation and limitations of these factors have been discussed [22]. These TEF values are used to convert the analytical results in TCDD or toxic equivalents (TEQs) where

$$TEQ = \sum ([PCB]_i \cdot TEF_i)$$

and i represents the individual PCB congener.

Calculated TEQs for the planar PCB congeners, in $pg\ g^{-1}$, in oyster tissues collected from Galveston and Tampa bays

as well as their totals are listed in Table 1. In Tampa and Galveston bays, the total TEQs ranged from 13.5 to 52.2 $pg\ g^{-1}$ and from 13.0 to 280 $pg\ g^{-1}$, respectively. The data indicate that, except for the sample collected near the Houston Ship Channel in Galveston Bay, the TEQs in oysters from Tampa and Galveston bays were similar. Oysters collected near the Houston Ship Channel in Galveston Bay were clearly the most toxic.

Mono- and di-ortho-PCB congeners, derivatives of planar PCB congeners, are relatively less toxic but far more abundant in environmental samples than their parent compound and might, therefore, have a significant toxic environmental impact. To assess the environmental significance of these congeners in terms of TCDD-like effects in oyster samples from Galveston and Tampa bays, the calculated 2,3,7,8-TCDD equivalents corresponding to congeners 105, 118, 128, and 138 were compared to those corresponding to planar congeners (Table 1). Contribution of congeners 105 plus 118 to the total TEQs was as high as 45.4%. In contrast, the contribution of di-ortho congeners to the total toxicity of the samples is negligible (<1.0%). The lesser toxicity of the di-ortho congeners is a consequence of their reduced TCDD-like activity rather than lower concentrations. Congeners 77, 126, 169, 105, and 118 accounted for over 90% of the total TEQs encountered in a variety of biota samples [8,10,23,24].

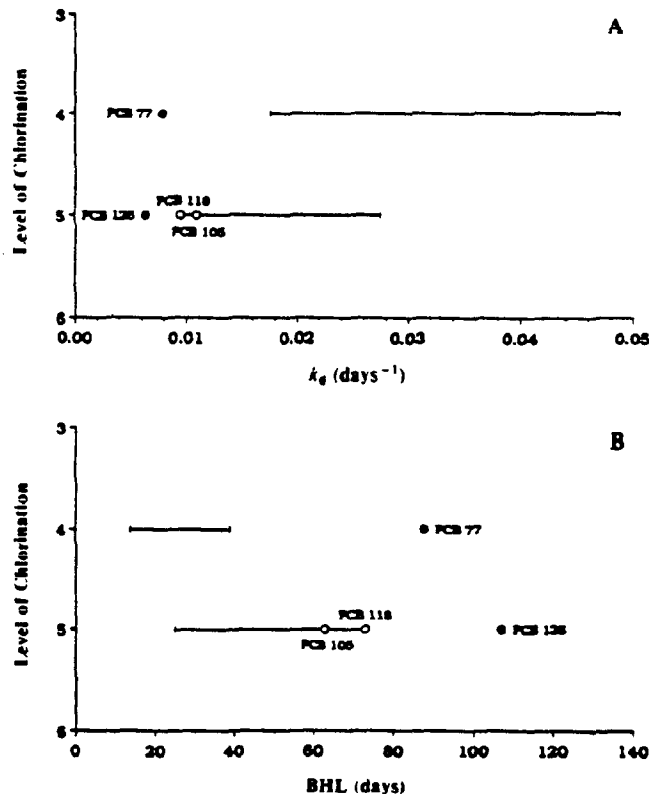


Fig. 2. Depuration constant (k_d) and biological half-lives (BHL) of planar congeners compared to ranges of values calculated for nonplanar PCBs. Values for selected mono-ortho-chlorine-substituted congeners relevant to this study are also shown.

Most of the relative PCB toxicity encountered during this study was associated with the presence of planar PCBs, particularly congener 126. In a recent study, Sericano et al. [25] reported that planar PCBs 77 and 126 were depurated from the oyster tissue at a significantly lower rate than other PCB congeners within the same level of chlorination. That report confirmed the findings of a previous study with transplanted mussels [7]. However, not only the planar PCB congeners but also their mono-ortho derivatives show slower depuration rates than the bulk of PCB congeners in the corresponding level of chlorination (Fig. 2). This might be of significant importance in projects such as the Mississippi oyster relaying effort designed to transplant oysters from polluted to clean waters for a period of time before harvesting them for human consumption [26]. Bohem and Quinn [27] reported that transplanting of shellfish from polluted to cleaner environments has been used as a means of increasing harvestable yields of the hard-shell clam (*Merccenaria mercenaria*) in Narragansett Bay, Rhode Island. However, oysters that are allowed to depurate in a clean environment might show lower concentrations of PCBs but still may retain significant amounts of the highly toxic congeners.

SUMMARY AND CONCLUSIONS

The total TEQs in oyster samples from the Gulf of Mexico were estimated from the concentrations of planar PCB congeners—i.e., 77, 126, and 169—and two mono-ortho-substituted PCB congeners—i.e., 105 and 118—using published TEF values. As it has been discussed in previous studies for a variety of biota samples, most of the relative PCB toxicity detected in oyster tissues was associated with these congeners. The slower depuration rates reported for these congeners compared to other PCBs within the same level of chlorination suggest that most of the toxicity would be retained by depurating oysters even though the total PCB concentrations might have significantly decreased. This might have a significant effect on the applicability of some of the shellfish industry practices such as oyster relaying.

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Reprint 3

**Distribution and Sources of Organic
Contaminants in Tidal River Sediments
of the Washington, D.C. Area**

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Distribution and Sources of Organic Contaminants in Tidal River Sediments of the Washington, D.C. Area.

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Organic contaminants in tidal river sediments

Abstract

Concentrations of aliphatic, aromatic and chlorinated hydrocarbons were determined from 45 surface-sediment samples taken from the Tidal Basin, Washington Ship Channel, and the Anacostia and Potomac rivers in Washington, D.C. In conjunction with these samples, selected storm sewers and outfalls also were sampled to help elucidate general sources of contamination to the area.

All of the sediments contained detectable concentrations of aliphatic and aromatic hydrocarbons, DDE, DDD, DDT, PCBs, and chlordanes (oxy, α , and γ -chlordane and cis+trans-nonachlor). Sedimentary concentrations of most contaminants were highest in the Anacostia River just downstream of the Washington Navy Yard, except for total chlordane which appeared to have upstream sources in addition to storm and combined sewer runoff. This area has the highest concentration of storm and combined sewer outfalls in the river. Potomac River stations exhibited lower concentrations than other stations. Total hydrocarbons (THC), normalized to the fine grain fraction (clay+silt, $< 63 \mu\text{m}$), ranged from 120 to $1900 \mu\text{g g}^{-1}$ fine grain. The hydrocarbons were dominated by the unresolved complex mixture (UCM) with total polycyclic aromatic hydrocarbons (PAHs) concentrations ranging from 4 to $33 \mu\text{g g}^{-1}$ fine grain. Alkyl-substituted compounds (e.g., C1 to C4 methyl groups) of naphthalene, fluorene, phenanthrene+anthracene, and chrysene series dominated the polycyclic aromatic hydrocarbons (PAHs). Polycyclic aromatic hydrocarbons, saturated hydrocarbons, and the unresolved complex mixture (UCM) distributions reflect mixtures of combustion products (i.e. pyrogenic sources) and direct discharges of petroleum products. Total PCB concentrations ranged from 0.075 to $2.6 \mu\text{g g}^{-1}$ fine grain, with highest concentrations in the Anacostia River. Four to six Cl-substituted biphenyls were the most-prevalent PCBs. Variability in

the PCB distribution was observed in different sampling areas, reflecting differing proportion of Arochlor inputs and degradation. The concentration of all contaminants was generally higher in sediments closer to known sewer outfalls, with concentrations of THC, PAHs, and PCBs as high as 6900, 620, and 20 $\mu\text{g g}^{-1}$ fine grain, respectively. Highest PCB concentrations were observed from two outfalls that drain into the Tidal Basin. Concentrations of organic contaminants from sewers draining to the Washington Ship Channel and Anacostia River had higher concentrations than sediments of the mid-channel or river. Sources of PCBs appear to be related to specific outfalls, while hydrocarbon inputs, especially PAHs, are diffuse, and may be related to street runoff.

Whereas most point source contaminant inputs have been regulated, the importance of non-point source inputs must be assessed for their potential addition of contaminants to aquatic ecosystems. This study indicates that in large urban areas, non-point sources deliver substantial amounts of contaminants to ecosystems through storm and combined sewer systems, and control of these inputs must be addressed.

Introduction

Currently existing National Oceanic and Atmospheric Administration (NOAA), National Status and Trends (NS&T), and Environmental Protection Agency (EPA) Environmental Monitoring and Assessment-Near Coastal (EMAP-NC) programs are concerned with determining current contaminant status of coastal areas of the United States. These programs are designed to provide an overview of the current status and long-term trends for relatively large geographical areas. However, there remains a need for specific studies to address questions of a more local concern. In order to reduce the input of contaminants to aquatic systems, such as the tidal system around Washington, D.C., regulations of point sources have been implemented. With the reduction of point source inputs, non-point sources such as storm water runoff now must be assessed as input sources of contaminants to aquatic systems.

The paper describes one portion of a study (see Velinsky et al. and Schlekert et al., this issue) to determine the distribution of sedimentary organic contaminants on a local scale in the Washington, D.C. area, employing validated analytical methods. Also, an important objective of this study was to establish the importance of combined and storm sewers as sources of contaminants to the sediments of the area. To accomplish this objective, selected storm and combined sewers were sampled, and organic contaminant distributions compared between sewer and river sediments.

Sampling and Analytical Methods

The study area (Fig. 1) and sampling design has been described in detail in Velinsky et al. (1993). Sediment samples were obtained from the Tidal Basin (TB), Washington Ship Channel (WSC), Kingman Lake (KL), Potomac River (PR) and Anacostia River (AR) in June 1991 (Fig. 1). Sediments taken directly in front of storm and combined sewer outfalls were also collected from the

Anacostia River, Washington Ship Channel, and Tidal Basin. In addition, selected sewers were sampled up-pipe (i.e. entering the sewer line via street manholes) from the outfall in these locations (Velinsky et al. 1993). To accomplish this, D.C. Department of Public Works sewer maps were used to select specific sewer lines that drain into each area. Also, at one station in the Tidal Basin and Potomac and Anacostia rivers, three separate samples of three grabs each were taken within a radius of approximately 5 m to assess small-scale spatial variability.

In the Potomac River, four stations were sampled from the mouth of Rock Creek to the confluence of the Anacostia and Potomac Rivers and the Washington Ship Channel (Fig. 1). We did not obtain samples from sewers that drain into the Potomac River. In the Washington Ship Channel, five stations were sampled along the eastern side of the channel. Seven stations were sampled in the Anacostia River, all on the northwestern side of the river outside the center channel.

Sediments were collected with a stainless steel petite-Ponar grab sampler (0.023 m²) rinsed with acetone at the beginning of each day. The upper 2 to 3 centimeters of sediment not in contact with the sides of the sampler were placed into a pre-cleaned pyrex-glass bowl. This process was repeated three times. Sediments were mixed with a pre-cleaned stainless steel spoon until homogeneous in both texture and color, placed into pre-baked (420 °C for 12 hours) glass jars, and covered with pre-baked aluminum foil. Between collections, the sampler was cleaned of any sediment and rinsed with ambient water at each station.

Grain size and total organic carbon determination are described in Velinsky et al. (1993). Sediments were extracted using the methods described in Wade et al. (1988). All internal standards (surrogates) were added to the samples prior to extraction and were used for quantification. Approximately 10 grams of freeze-dried sediment were soxhlet-extracted with methylene chloride.

The solvent was concentrated to approximately 20 ml in a flat-bottomed flask equipped with a three-ball Snyder column condenser. The extract was then transferred to Kuderna-Danish tubes, which were heated in a water bath (60°C) to concentrate the extract to a final volume of 2 ml. During concentration of the solvent, dichloromethane was exchanged for hexane.

The extracts were fractionated by alumina:silica gel (80-100 mesh) open column chromatography. Silica gel was activated at 170°C for 12 hours and partially deactivated with 3% (v/w) distilled water. Twenty grams of silica gel were slurry packed in dichloromethane over 10 grams of alumina. Alumina was activated at 400°C for four hours and partially deactivated with 1% (v/w) distilled water. The dichloromethane was replaced with pentane by elution, and the extract was applied to the top of the column. The extract was sequentially eluted from the column with 50 ml of pentane (aliphatic fraction) and 200 ml of 1:1 pentane- dichloromethane (aromatic-pesticide fraction). The fractions were then concentrated to 1 ml using Kuderna-Danish tubes heated in a water bath at 60°C. Each set of ten samples included a procedural blank and a spiked sample that were carried through the entire analytical procedure.

Aliphatic hydrocarbons were analyzed by gas chromatography in the splitless mode using a flame ionization detector (FID). A 30-m x 0.32-mm I.D. fused silica column with DB-5 bonded phase (J&W Scientific Inc. or equivalent) was used, with the chromatographic conditions providing baseline resolution of the n-C₁₇/pristane and n- C₁₈/phytane peak pairs. The five calibration solutions were in the range of 1.25 to 50 µg ml⁻¹. The internal standards (surrogates) for the aliphatic hydrocarbon analysis were deuterated n-alkanes with 12, 20, 24 and 30 carbons, and were added at approximate 10 times the method detection limit.

Aromatic hydrocarbons were separated and quantified by gas chromatography-mass

spectrometry (GC-MS) (HP5890-GC and HP5970-MSD). The samples were injected in the splitless mode onto a 0.25 mm x 30 m (0.32 μ m film thickness) DB-5 fused silica capillary column (J&W Scientific Inc. or equivalent) at an initial temperature of 60°C and temperature programmed at 12°C min⁻¹ to 300°C and held at the final temperature for 6 minutes. The mass spectral data were acquired using selected ions for each of the PAH analytes. The GC-MS was calibrated by injection of a standard component mixture at five concentrations ranging from 0.01 ng/ μ l to 1 ng/ μ l. Sample component concentrations were calculated from the average response factor for each analyte. Analyte identifications were based on correct retention time of the quantitation ion (molecular ion) for the specific analyte and confirmed by the ratio of the confirmation ion.

A calibration check standard was run three times during the sample runs (beginning, middle and end), with no more than 6 hours between calibration checks. The calibration check was confirmed to maintain an average response factor within 10% for all analytes, with no one analyte greater than 25% of the known concentration. With each set of samples, a laboratory reference sample (oil solution) was analyzed to confirm GC-MS system performance. The internal standards (surrogates) for the PAH analysis were d₈-naphthalene, d₁₀-acenaphthene, d₁₀-phenanthrene, d₁₂-chrysene, and d₁₂-perylene, and were added at concentrations similar to that expected for the analytes of interest.

The pesticides and PCBs were separated by gas chromatography in the splitless mode using an electron capture detector (ECD). A 30-m x 0.32-mm I.D. fused silica column with DB-5 bonded phase (J&W Scientific or equivalent) was used. Four calibration solutions containing the pesticides and the PCBs were used to generate a non-linear line fit with calibration standards in the range of 5 to 200 ng ml⁻¹. The internal standards (surrogates) for pesticide and PCB analysis, added prior to

extraction, were DBOFB (dibromooctafluorobiphenyl), PCB-103, and PCB-198. The chromatographic conditions for the pesticide-PCB analysis were 100°C for 1 min, then 5°C min⁻¹ to 140°C, hold for 1 min, then 1.5°C min⁻¹ to 250°C, hold for 1 min, and then 10°C min⁻¹ to 300°C and a final hold of 5 min.

Results and Discussions

Sedimentary hydrocarbons

Sedimentary hydrocarbons concentrations were variable throughout the study area, probably due to transport processes, biological and chemical differences between individual compounds (i.e., water solubility, volatility, and weathering and microbial degradation rates), and the differences in input sources of these compounds. Total hydrocarbons concentrations (THC) in the Potomac River sediments ranged from 110 to 167 $\mu\text{g g}^{-1}$ (Table 1). The highest concentration was at station PR-1 which is located near the mouth of Rock Creek (Fig. 1). In the Potomac River, the UCM was the dominant THC component, averaging $84 \pm 0.04\%$ of the THC. The polycyclic aromatic hydrocarbon (PAHs) concentration are of particular interest because they have been shown to have a significant effect on the mortality, abundance, and diversity of benthic organisms (Landrum et al. 1991; Kennish 1992). Sediment concentrations were highest at PR-1 (29 $\mu\text{g g}^{-1}$) compared to other river, basin, or channel sediments (excluding outfall or sewer sediment). Stations PR-2, PR-3, and PR-4(a,b,c) had uniform PAH concentrations, averaging $3.6 \pm 0.4 \mu\text{g g}^{-1}$ (n=5, station PR-4 was sampled in triplicate). The higher concentrations of both PAHs and the UCM indicate a greater amount of anthropogenic hydrocarbons at PR-1, most likely due to runoff from Rock Creek, which drains through the more residential center of Washington, D.C.

In the Tidal Basin, THC and PAH ranged from 169 to 613 $\mu\text{g g}^{-1}$ and from 0.4 to 11.6 $\mu\text{g g}^{-1}$

, respectively. The higher concentrations of PAH at TB-1 and TB-1.5 were associated with large storm sewer and vehicular traffic on Kutz Bridge near TB-1.5. THC concentrations ranged from 120 to 467 $\mu\text{g g}^{-1}$ in Washington Ship Channel (WSC) sediments. The highest sediment concentrations were at stations WSC-1, WSC-2, and WSC-3, located at the upper end of the channel. As in the other areas, THCs were dominated by the UCM (UCM/THC $\geq 95\%$), suggesting that the THCs were composed mainly of weathered petroleum products (Farrington 1980). Sediment PAH concentrations were fairly uniform throughout the channel with an overall average of $7.0 \pm 1.0 \mu\text{g g}^{-1}$ ($n=5$).

To assess geographical trends of hydrocarbons in the Anacostia River, concentrations of organic compounds are presented along a transect from KL-5, at the entrance to Kingman Lake in the AR, to PR-4, which is located at the confluence of the Anacostia and Potomac rivers (Fig. 1; Table 1). This transect includes WSC-6, located at the confluence of the AR and the WSC. Along the river, at AR-4, which is located just upstream of the South Capitol Street Bridge (Fig. 2), concentrations of THC and PAHs reached a maximum of 1600 $\mu\text{g g}^{-1}$ and 28 $\mu\text{g g}^{-1}$, respectively. From AR-4 to PR-4, a substantial decrease occurred in the concentrations of both THC and PAHs. At the most downstream station (PR-4A), concentrations of THC and PAHs, 126 $\mu\text{g g}^{-1}$ and 4.4 $\mu\text{g g}^{-1}$, respectively, were some of the lowest measured in this study. Similar trends also were found for trace metals (e.g., Pb and Cd; Velinsky et al. 1993), indicating a substantial local source of sediment contamination near the Washington Navy Yard and the South Capital Street Bridge (Fig. 1).

Several stations were sampled and analyzed in triplicate to assess the small-scale spatial variability. Triplicate samples of three grabs each were taken within approximately 5 m of each other. The percent relative standard deviation (%RSD; $\pm \text{SD}/\text{mean} \times 100$) for THC, SHC, and the

UCM was all generally $< \pm 15\%$ for the Potomac River (PR-4) and the Anacostia River (AR-5). In the Tidal Basin (TB-5), total PAH concentrations agreed to within $\pm 5\%$ RSD ($n=3$); however, concentrations of THC, SHC and UCM had higher concentrations for sample TB-5b. It is unclear why the THC, SHC, and UCM were elevated in TB-5b. Trace metals, TOC, and grain size data (Velinsky et al. 1993) were not elevated for TB-5b compared to TB-5a,c. Due to the close agreement between TB-5a and TB-5c for both the SHC and UCM, the data for TB-5b is not included in the average and further discussions. These results, along with the TOC and grain size data (Velinsky et al. 1993), indicate that the variability of the "local" area is smaller than some of the geographic trends between the various study areas.

One of the objectives of this study was to evaluate sources of organic contaminants to river sediments in the Washington, D.C. area. Sediment samples were collected at the outfalls of selected storm and combined sewers (IDs with the prefix O; Table 1) in the Tidal Basin, Washington Ship Channel, and Anacostia River. Sediments also were taken from combined and storm sewers (IDs with the prefix S; Table 1) that drain into these areas. Sediment hydrocarbons concentrations for rivers, outfalls, and sewers were divided by the fraction of fine grain sediment ($< 63 \mu\text{m}$) in each sample (Velinsky et al. 1993).

Total hydrocarbons and total PAHs concentrations from outfall and sewer sediments from the Tidal Basin and Washington Ship Channel were substantially elevated compared to sediments collected away from the outfalls (Fig. 3). The PAH concentrations in outfall samples ranged from 10 to 620 $\mu\text{g g}^{-1}$ fine grain, with highest concentrations from one site in the WSC. These concentrations were substantially higher than those found in mid-basin or channel sediments. This suggests that a dominant source of hydrocarbons to the basin and channel is runoff from numerous streets and

highways in the area via the storm sewer system (there are no combined sewers in these areas). The distribution of THC and PAHs at the outfalls indicated no specific storm sewer as the predominate source of hydrocarbons to these areas, as opposed to the trace metal data, notably Pb, which did indicate specific outfalls (e.g., OTB-3&4, OAR-3) as major sources (Velinsky et al. 1993). It appears that the input of hydrocarbons to the basin is diffuse, and may be related to the overall vehicular traffic in the surrounding area.

While the gradients between outfall and sediment samples indicate the source of hydrocarbons is from street runoff, the numerous marinas that border the eastern side of the WSC could also contribute hydrocarbons to channel sediments. The input of hydrocarbons would be related to boating activities, fuel spills, and engine exhaust, as well as from creosote-treated pilings used for the construction of these marinas (Vouldrias and Smith 1986; McGee et al 1993).

In the Anacostia River (AR), five outfall and four sewer samples were obtained, allowing a more comprehensive analysis of the sediment hydrocarbon distribution (Fig. 4). Of the four sewers sampled, two are storm sewers (SAR-5 and SAR-6), and two are combined sewers (SAR-2 and SAR-3); all were sampled as close to the river as possible. In most cases, the concentrations of THCs and PAHs were highest in the sewer samples compared to either the outfall or sediment samples (Fig. 4). A comparison was made between hydrocarbon concentrations of three groups of river, outfall, and sewer samples within the AR (Fig. 4). The material collected in the sewer is a possible source of hydrocarbons at the outfall, and thus would most directly affect the sediments in the river at the station closest to the outfall. Total hydrocarbons and PAH concentrations were higher from all sewer samples compared to their respective river samples (Fig. 4). This trend is particularly evident in the series located near the Washington Navy Yard (i.e., series AR-4, OAR-3, and SAR-5).

Concentrations of THC decreased from 4500 at SAR-5 to approximately 2000 $\mu\text{g g}^{-1}$ fine grain at both OAR-3 and AR-4 (Fig. 4), while PAH concentrations decreased by a factor of 5 between SAR-5 and AR-4. The decrease in THC and PAH concentrations in river sediments compared to sewer samples may be due to both degradation and dilution with sediments having lower hydrocarbon concentrations.

These results indicate that a major source of hydrocarbon contamination to the sediments of the Anacostia River may be street runoff through the combined and storm sewer system of the area. Gavens et al. (1982) showed that in an urban catchment basin near London (G.B.), up to a 3 fold increase in sedimentary PAHs occurred due to urban runoff. Street dust, including material from tires, road asphalt, and crankcase oils, are possible sources of hydrocarbons in this runoff. Wakeham et al. (1980) compared the PAH content of various lake sediments in Switzerland to various urban source materials, and concluded that street dust (e.g., asphalt and tire, and crankcase drippings) was a major source of hydrocarbons to the sediments. Other sources, such as atmospheric deposition and direct oil spills to the river, may be important, but the extreme concentration gradient between river, outfall, and sewer sediment samples suggests that urban runoff is a major source. Samples taken around station AR-4, near the Washington Navy Yard, indicate that this may be the most severely impacted area in the Anacostia River, and may be the most affected by runoff from the urban area of Washington, D.C.

Molecular Distribution of Hydrocarbons

Total sedimentary hydrocarbons consist of saturated hydrocarbons (SHC), polycyclic aromatic hydrocarbons (PAH), and the unresolved complex mixture (UCM). The UCM contains co-eluting

compounds that are not resolved by current capillary gas chromatographic techniques, and are thought to be mainly alicyclic hydrocarbons. Saturated hydrocarbons are the sum of normal alkanes from $n\text{-C}_{10}$ to $n\text{-C}_{24}$ including the isoprenoids pristane and phytane, and PAHs are the sum of 44 individual or groups of aromatic hydrocarbons. While PAHs are potentially more harmful to aquatic organisms than SHC or UCM, the molecular distribution and abundance of the UCM, SHC, and PAH provides information concerning the sources and transformations of hydrocarbons (Farrington 1980; Hites et al. 1980; Wakeham et al. 1980; Boehm and Farrington 1984; Boehm 1984; Pruell and Quinn 1985).

The UCM accounted for the majority of THC in sediments, outfall and sewer samples, with minor contributions of both SHCs and PAHs. For most sediments the UCM accounted for $\geq 95\%$ of the THC with little variation between sites. The abundance of the UCM at all collection sites indicates that weathered petroleum products are a major component of hydrocarbon contamination in this area. In the Potomac River however, the UCM comprised $\leq 90\%$ of the SHC, indicating less of a contribution of weathered petroleum hydrocarbons. The source of the UCM in all areas is most likely runoff from streets and highways, although direct discharge of oil (i.e., small spills) cannot be ruled out (Eganhouse and Kaplan 1981a; 1981b; Hoffman et al. 1983; 1984; Brown et al. 1985). While the concentration and presence of the UCM indicates a weathered-petroleum hydrocarbon source, the molecular distribution of PAHs can give an indication of the relative contribution of hydrocarbons from petroleum versus combustion sources.

Low versus high molecular weight PAHs (i.e., LMW and HMW PAHs) are indicative of the input sources of hydrocarbons (Farrington 1980; Boehm and Farrington 1984). Low molecular weight PAHs are defined as 2 to 3 benzene ring compounds, including naphthalenes, anthracenes, phenanthrenes, and dibenzothiophenes. High molecular weight PAHs, with 4 to 5 benzene rings,

include compounds such as fluoranthenes, chrysenes, benzo[a]pyrene and dibenz[ah]anthracene. A predominance of LMW over HMW PAHs indicates an oil source of hydrocarbons (Farrington 1980; Boehm and Farrington 1984). Due to weathering and degradation processes, with time LMW PAHs would decrease in abundance relative to HMW PAHs. Also, the combustion of petroleum yields PAHs with more HMW compounds.

In most sediments from this study, LMW PAH accounted for approximately 35% of the total PAH (Velinsky et al 1992). In the Anacostia River, at stations AR-4 and SAR-5 however, LMW PAH accounted for 60% and 90% of the total PAHs, respectively. Storm sewer SAR-5 empties into the river near station AR-4 at the outfall OAR-3. Low molecular weight hydrocarbons accounted for only 40% of the total PAHs at station OAR-3. These results indicate a distinct source of petroleum-derived hydrocarbons (e.g., oil) to the area just south of the Washington Navy Yard near the South Capitol Street Bridge.

Substantial quantities of unsubstituted PAHs were found in all river, outfall, and sewer sediments analyzed. Major compounds include alkylated phenanthrene-anthracene, fluoranthene, pyrene, benz[a]anthracene, and benzopyrenes. Concentrations of alkylated fluoranthene-pyrene ranged from 0.56 to 5.3 $\mu\text{g g}^{-1}$, benz[a]anthracene from 0.11 to 0.93 $\mu\text{g g}^{-1}$, and benzo[a+e]pyrenes from 0.23 to 1.7 $\mu\text{g g}^{-1}$ for all river sediment samples. Higher concentrations were found in outfall and sewer samples (Velinsky et al. 1992). The abundance of individual HMW PAH compounds in most samples suggests that combustion products are also a source of the PAHs to the sediments of this area (Youngblood and Blumer 1975).

The variations in individual PAH compounds reflect a mixture of combustion products (i.e., pyrogenic sources) and direct discharge of petroleum products. These distributions are similar to

other urban areas (Farrington and Quinn 1973; Wakeham et al. 1980; Hoffman et al. 1983; 1984; Eganhouse and Kaplan 1981b; Brown et al. 1985). Specific areas that indicate increased combustion inputs of hydrocarbons include station PR-1 near Rock Creek, stations WSC-1, 2, and 3, and the area around AR-4 (Velinsky et al. 1992). Only in the Anacostia River, near the Washington Navy Yard (i.e., AR-4), are direct inputs of petroleum a more significant component of the sediments.

Chlorinated Hydrocarbons

The concentration of a selected suite of chlorinated hydrocarbons were determined as part of this study. Sediment concentrations of total chlordanes (sum of oxy-, γ -, and α -chlordane and cis+trans-nonachlor), total DDT (sum of 2,4' + 4,4' forms of DDT, DDD, and DDE), and total PCBs ranged from 5 to 150, 7 to 160, and 70 to 2200 ng g⁻¹, respectively, for river, basin or channel sediments (Table 2). The highest sedimentary total chlordanes levels from the Potomac River (43 ng g⁻¹) were near Rock Creek at station PR-1, with lower concentrations downstream. This site also exhibited high concentrations of total DDT and PCBs compared to the other sampling sites in the Potomac River. The highest concentrations of total chlordanes, total DDT, and PCBs in the Tidal Basin were found at stations TB-1 and TB-1.5. These sites are located near the large storm sewer outfall that drains along Constitution Avenue and the Mall of the Smithsonian Institution. The sediment concentrations of total DDT at these stations, 160 and 170 ng g⁻¹, were some of the highest measured in this study. Concentrations of total chlordanes, DDT, and PCBs in the Washington Ship Channel were intermediate compared to the other study areas, with no distinct geographical distribution (Table 2).

Higher concentrations of total chlordanes were determined in the Kingman Lake area (e.g.,

maximum at KL-4 of 150 ng g^{-1}) and upper Anacostia River (Fig. 2) compared to farther downstream. Concentrations decreased to approximately 27 ng g^{-1} at PR-4A, located just south of Hains Point in the Potomac River. This distribution, suggests a possible input source within or upstream of the Kingman Lake area. In contrast, concentrations of both total DDT, PCBs, and hydrocarbons reached maximum levels farther downstream in the Anacostia River at station AR-4. Sediment concentrations of total DDT and PCBs were 124 and 2200 ng g^{-1} , respectively, at AR-4. Numerous storm and combined sewers drain into this area, and these levels are probably a result of these sources (see below). This location also has elevated concentrations of trace metals (Velinsky et al. 1993), THC's, and PAH's. Below the South Capital Street Bridge and the Washington Navy Yard (i.e., AR-4), concentrations of all sediment contaminants decreased to baseline levels. The distribution of total chlordane indicates different input sources to the Anacostia River compared with other organic and inorganic contaminants.

Concentrations of total chlordane, DDT, and PCBs in outfalls of the Tidal Basin and Washington Ship Channel reached levels of 260 , 4200 and 18000 ng g^{-1} fine grain respectively, and are substantially higher than those determined in the mid-basin or channel sediments (Fig. 5). Outfalls OTB-3 and OTB-4 had extremely elevated concentrations in the Tidal Basin. The sewer (STB-2), taken on two separate occasions, had concentrations of total chlordane, DDT, and PCBs only slightly elevated compared to basin sediments. This sewer is a sanitary sewer running along 15th St., S.W., servicing the Bureau of Engraving and Printing and the Department of Agriculture. The material in this sewer line would most likely not impact the Tidal Basin, and would eventually be sent to Blue Plains Wastewater Treatment facility for treatment and disposal. Total chlordane, DDT, and PCB outfall sediment concentrations in the Washington Ship Channel were as high as 600 , 2100 ,

and 5200 ng g⁻¹ fine grain, respectively. Highest total chlordane and DDT concentrations were found at OWSC-3, while total PCB concentrations were highest at all three upstream outfalls (i.e., OWSC-2 to OWSC-R1; Fig. 5).

A substantial concentration gradient between sewers, outfalls and sediments of the Anacostia River was observed for total chlordane, DDT, and PCBs (Fig. 6). Concentrations in this series were as high as 660, 400, and 6400 ng g⁻¹ fine grain for total chlordane, DDT, and PCBs, respectively. As with non-chlorinated hydrocarbons, a large decrease in concentrations was found between the sewer, outfall, and sediments near station AR-4 (i.e., SAR-5 >> OAR-3 >> AR-4) (Fig. 6). Similar decreases were observed in varying degrees for the other river, outfall, and sewer sediment series within Anacostia River (Fig. 6). These data indicate that street and land runoff, as well as possible combined sewer overflows, are sources of total chlordane, DDT, and PCBs to the sediments of the Anacostia River.

Persistence of PCBs in aquatic sediments is due to their slow rate of degradation and vaporization, low water solubility, and partitioning to particles and organic carbon (Kennish 1992). Bacteria degrade PCBs, with the rate dependent on the position and degree of chlorination of the biphenyl ring (Reutergardh 1980; Abramowicz et al. 1993; Rhee et al. 1993). Interestingly, the PCB congener distribution patterns are not similar among sediments of this study area (Velinsky et al. 1992). In the Tidal Basin and Potomac River, congeners with six and seven chlorine substitutions dominated, while congeners with four to six chlorines were the major component of the PCBs of Washington Ship Channel and Anacostia River sediments. These results suggest two distinct sources of PCB contamination in this study area. However, the selective degradation of PCBs with lower chlorine contents can not be ruled out as the cause of the different distributions (Reutergardh 1980

and others).

Sources of the pesticide DDT measured in the present study are elusive. Banned in 1972, and with an approximate environmental half-life of 10 to 20 years (NOAA 1989; Woodwell et al. 1971; Sericano et al. 1990), its detection, along with its breakdown products (i.e., DDE+DDD) in sediments, is to be expected. Generally, (2,4' + 4,4') DDE accounted for the greatest abundance of the three forms of DDT, with approximately 70 to 90% of the total DDT in sediments as the sum of DDE and DDD (2,4' + 4,4') forms. This distribution indicates an active degradation of DDT in the sediments and/or inputs of already degraded DDT to the area. DDT can be degraded to DDD by micro-organisms and phytoplankton or to DDE via dehydrochlorination produced by biotic or abiotic decomposition reactions (Fries 1972; Addison 1976; Gerlach 1981).

In all outfalls and sewers sampled in the Anacostia River, along with specific ones in the Tidal Basin and Washington Ship Channel, (2,4' + 4,4') DDT accounted for approximately 40 to 60% of the total DDT, and with the extreme concentrations measured at these sites, detrimental biological effects could occur. The large sedimentary concentrations of (2,4' + 4,4') DDT at outfalls and in sewers is interesting given the apparent lack of any definitive recent inputs. It might be expected that DDT would have been flushed through the sewer system 20 years after its ban. Schmitt et al. (1985) suggested that DDT may be a contaminant in other pesticide mixtures; however, the study of Schmitt et al. (1985) was conducted in cotton farming areas in the southwest U.S. and may not be applicable to the District. Alternatively, it is possible that re-exposed soils from construction projects could introduce DDT to the environment.

Technical chlordane is a pesticide, used for termites and cutworms, that is a mixture of approximately 140 compounds. Due to its known health effects, sale of technical chlordane was

halted in 1988 after step-wise control of its uses. Alpha (α)- and gamma (γ)-chlordane are the two main components of technical chlordane. The different forms and breakdown products of technical chlordane were found at all locations with the exception of oxy-chlordane, which was found in only nine samples. Generally, oxy-chlordane was found in detectable concentrations in specific outfall and sewer sediment samples in the Tidal Basin, Washington Ship Channel, and Anacostia River, and accounted for 3 to 14% (n=9) of the total chlordane. Oxy-chlordane is a breakdown product of chlordane and is thought to be more toxic than the other forms of chlordane. Throughout the DC area, γ -chlordane was the major chlordane found in this study area with lesser amounts of α -chlordane and cis+trans-nonachlor (Velinsky et al. 1992).

Comparisons to other Studies

Comparisons of the data from this study to other studies is not straightforward. The variable nature of the sediments (i.e., grain size, organic carbon, etc.) are often ignored or can not be accounted for from other studies that did not report bulk sediment characteristics. Also, the selection of specific studies can bias the interpretation between data sets. For this reason, only data from the Chesapeake Bay and Delaware Bay will be utilized to give a regional assessment of sediment contamination.

Concentrations of selected organics from the mid-Atlantic region are compared in Table 3. In the present study, station AR-4 in the Anacostia River exhibited the highest concentrations, while the Potomac River sediments have some of the lower concentrations (excluding outfall or sewer sediment samples). The concentration of total PCBs in the Baltimore Harbor and Schuylkill River (Philadelphia, PA.) are much higher than the Washington, D.C. area. For all groups of organics, concentrations

measured in this study are higher than those from the mainstem Chesapeake Bay, again reflecting the effect of urban environments on adjacent sediments. Compared to other studies, the sediments of the tidal freshwater Washington, D.C., area are moderately to highly contaminated, with the most severely impacted area located in the Anacostia River near station AR-4.

Summary and Conclusions

The geographic and spatial trends for sedimentary organic reveal specific areas of concern within the tidal freshwater section of the upper Potomac estuary. These locations are show increased sediment concentrations of organic contaminants relative to adjacent locations, and within the entire study area of the Potomac and Anacostia rivers. In many cases, both trace metals (see Velinsky et al. 1993) and organics exhibit the same geographic trend. Substantial concentrations of organics such as hydrocarbons (e.g., PAHs), PCBs, and DDTs were observed in many areas, such as near the Washington Navy Yard (AR-4), near the mouth of Rock Creek in the Potomac River (PR-1), and upper Washington Ship Channel (WSC-1 to WSC-3). Concentration gradients between sewer, outfall, and river sediment samples strongly suggest that urban runoff is a major non-point source of these contaminants to the sediments. For certain constituents like THC and PAH, the outfall sediment concentrations indicate a diffuse distribution related to the ubiquitous nature of their sources (i.e., fossil fuel combustion, crankcase oils etc.), while other contaminants, such as PCBs, have distributions that suggest more of a source input through specific outfalls. The distribution of total chlordane, which was markedly different than other organic contaminants, suggests inputs upstream of the Washington, D.C. area. Also, the analyses of a limited number of benthic clams (*Corpicula* sp.) from selected sites indicates that the contaminants found in the sediments are bioavailable (Velinsky

et.al. 1992) and may cause a biological response (Schlekat et al. 1993).

Large urban areas are non-point sources and deliver substantial amounts of organic contaminants to ecosystems through their sewer system runoff. With the decrease in point source contaminant inputs due to effective regulation, non-point source inputs must be assessed for their potential addition of contaminants to aquatic systems. Also, the toxicity of these sediments must be considered when making management decisions that might release or redistribute these contaminants. Organic contaminant concentrations found in this urban area are moderate to high, and may exert adverse effects on local ecosystems (see Schlekat et al. 1993).

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Table 1. Sedimentary concentrations of hydrocarbons from the various study areas*.

Sta. ID.	PAH	SHC	UCM	THC
<u>Kingman Lake</u>				
KL-1	16.1	17.7	911	944
KL-2	15.3	14.9	1000	1030
KL-3	14.2	15.2	2090	2120
KL-4	10.3	15.9	1270	1300
KL-5	9.8	27.9	852	890
<u>Anacostia River</u>				
AR-1	14.4	12.7	902	929
AR-2	15.1	22.1	1370	1410
AR-3	13.2	12.1	856	881
AR-4	28.3	31.0	1540	1590
AR-5A	9.6	10.7	784	804
AR-6	5.7	6.2	350	362
OAR-1	23.7	26.2	1460	1510
OAR-2	28.6	21.6	876	926

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Sta. ID.	PAH	SHC	UCM	THC
OAR-3	23.6	14.8	394	432
OAR-4	19.1	15.5	1190	1230
OAR-6	36.9	6.1	117	160
OAR-R1	11.5	7.5	581	600
SAR-2	32.1	9.7	469	511
SAR-3	5.8	2.2	393	401
SAR-5	39.6	25.4	901	966
SAR-6	8.7	7.5	500	516
<u>Washington Ship Channel</u>				
WSC-1	7.2	8.4	385	400
WSC-2	7.2	8.8	451	467
WSC-3	6.3	6.2	430	443
WSC-5	8.7	6.1	106	121
WSC-6	5.6	17.3	281	304
OWSC-1	9.9	66.2	604	680
OWSC-2	44.2	36.1	952	1030
OWSC-3	130.0	6.6	293	430

Sta. ID.	PAH	SHC	UCM	THC
OWSC-R1	78.3	54.5	4080	4210
SWSC-2	4.4	3.7	555	563
<u>Potomac River</u>				
PR-1	29.1	5.9	132	167
PR-2	3.6	13.5	110	127
PR-3	3.7	13.4	93	110
PR-4A	3.6	13.0	109	126
<u>Tidal Basin</u>				
TB-1	11.6	3.7	380	395
TB-1.5	9.8	14.8	595	620
TB-2	3.8	3.5	162	169
TB-3	8.7	18.3	300	327
TB-4	4.9	12.2	439	456
TB-5A	4.8	19.5	954	978
TB-6	3.8	3.8	171	179
OTB-1-1	6.9	1.2	86	94
OTB-1-2	8.0	10.7	285	304

Sta. ID.	PAH	SHC	UCM	THC
OTB-2	10.6	3.0	143	157
OTB-3	5.0	5.9	449	460
OTB-4	11.6	22.1	629	663
OTB-5	10.6	22.0	739	771
STB-2-1	9.0	12.1	1480	1500
STB-2-2	8.6	11.3	965	985

*Concentrations in μg per gram dry weight. PAH-polycyclic aromatic hydrocarbons; SHC-saturated hydrocarbons; UCM-unresolved complex mixture; THC-total hydrocarbons.

Station IDs. starting with the prefix (O) indicate samples that were taken directly in-front of an sewer outfall, while the prefix (S) indicates samples that were taken in a sewer.

Stations AR-5, PR-4 and TB-5 were sampled and analyzed in triplicate and the average value is reported.

Table 2. Concentrations of total chlordane, DDT, and PCBs from the various study areas.*

Sta. ID.	Chlordane	DDT	PCB
<u>Kingman Lake</u>			
KL-1	96	36	650
KL-2	110	65	530
KL-3	120	61	460
KL-4	150	76	520
KL-5	140	78	660
<u>Anacostia River</u>			
AR-1	140	78	710
AR-2	91	56	510
AR-3	110	77	770
AR-4	89	120	2200
AR-5A	58	55	490
AR-6	28	29	220
OAR-1	120	110	380

Sta. ID.	Chlordane	DDT	PCB
OAR-2	120	100	1300
OAR-3	33	44	840
OAR-4	93	261	480
OAR-6	38	320	340
OAR-R1	23	54	140
SAR-2	5	58	89
SAR-3	26	23	75
SAR-5	140	69	790
SAR-6	17	26	1500
<u>Washington Ship Channel</u>			
WSC-1	14	42	390
WSC-2	19	36	330
WSC-3	18	30	310
WSC-5	28	36	300
WSC-6	17	15	140
OWSC-1	39	51	990
OWSC-2	64	58	3200

Sta. ID.	Chlordane	DDT	PCB
OWSC-3	130	450	880
OWSC-R1	30	150	2800
SWSC-2	5	7	260
<u>Potomac River</u>			
PR-1	42	100	270
PR-2	7	10	68
PR-3	5	7	73
PR-4A	9	11	70
<u>Tidal Basin</u>			
TB-1	25	160	610
TB-1.5	17	170	500
TB-2	6	23	110
TB-3	14	88	250
TB-4	8	76	240
TB-5A	8	39	190
TB-6	7	29	150
OTB-1-1	4	58	110

Sta. ID.	Chlordane	DDT	PCB
OTB-1-2	14	120	400
OTB-2	7	150	240
OTB-3	10	75	1300
OTB-4	50	800	3400
OTB-5	15	80	380
STB-2-1	10	43	730
STB-2-2	38	91	290

*Concentrations in ng per gram dry weight. Station IDs. starting with the prefix (O) indicate samples that were taken directly in-front of an outfall, while the prefix (S) indicates samples taken in a sewer. Stations AR-5, PR-4, and TB-5 were sampled and analyzed in triplicate, these data are the average.

Chlordane is the Σ of $\alpha + \gamma$ -chlordane and cis+trans + nonachlordane;

DDT is the Σ of DDD + DDE + DDT (2,4' + 4,4' forms); PCB is the Σ of

77 congeners.

Table 3. Comparison of selected organic data from various studies in the region.*

PCBs	PAHs	DDT	Chlordanes	Location	Source
68 - 2203	4 - 29	7 - 160	5 - 153	Washington, D.C.	This Study ^b
4 - 80000	ND ^c	ND	ND	Baltimore Harbor	EPA (1987)
<100 - 2400	ND	<10 - 100	0 - 70	Schuylkill River, PA.	EPA (1987)
ND	ND	ND	ND	Potomac Estuary	MDE (unpub. data) ^d
7 - 96	0.03 - 1.11	0.2 - 4.8	0.2 - 2.4	Lower Ches. Bay	NOAA (1991)
1 - 100	0.04 - 0.83	0.2 - 6.2	0.1 - 10	Middle Ches. Bay	NOAA (1991)
1 - 450	0.07 - 5.3	4.9 - 21.7	0.6 - 8.1	Upper Ches. Bay	NOAA (1991)

* Concentrations of PCBs, DDTs, and chlordane are in ng per gram, and PAHs are in μg per gram dry weight. ^bOnly river or basin sediment samples are presented for this study. ^cND - No data. ^dMaryland Department of the Environment.

Figure Captions:

Figure 1. General study area indicating the locations of Tidal Basin, Washington Ship Channel, Kingman Lake, and the Potomac and Anacostia rivers. Arrows located around the shoreline indicate locations of outfall and sewer samples.

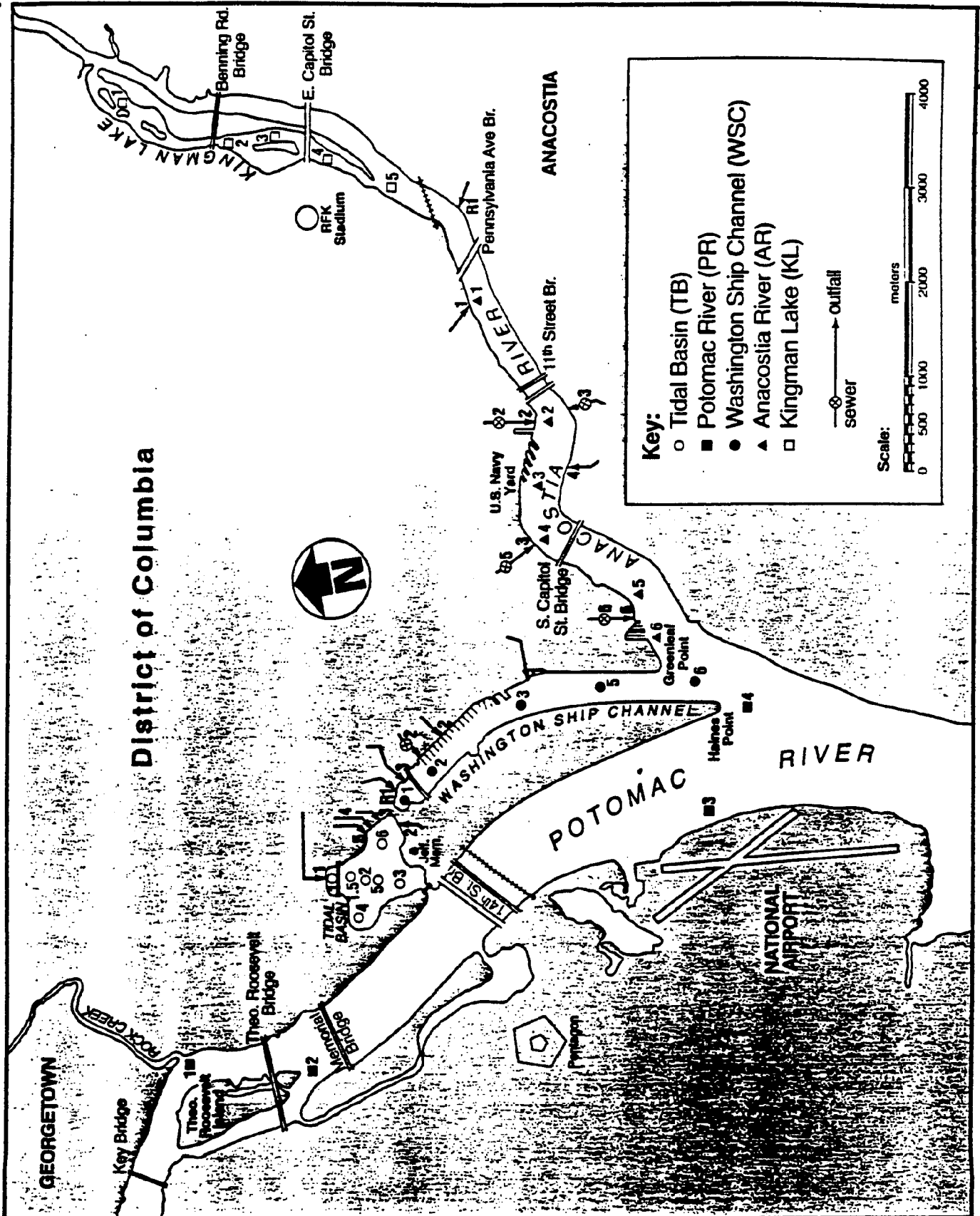
Figure 2. Hydrocarbons and chlorinated-hydrocarbons in sediments of the Anacostia River. Transect is from the mouth of Kingman Lake (KL-5) to the confluence of the Anacostia and Potomac rivers (PR-4).

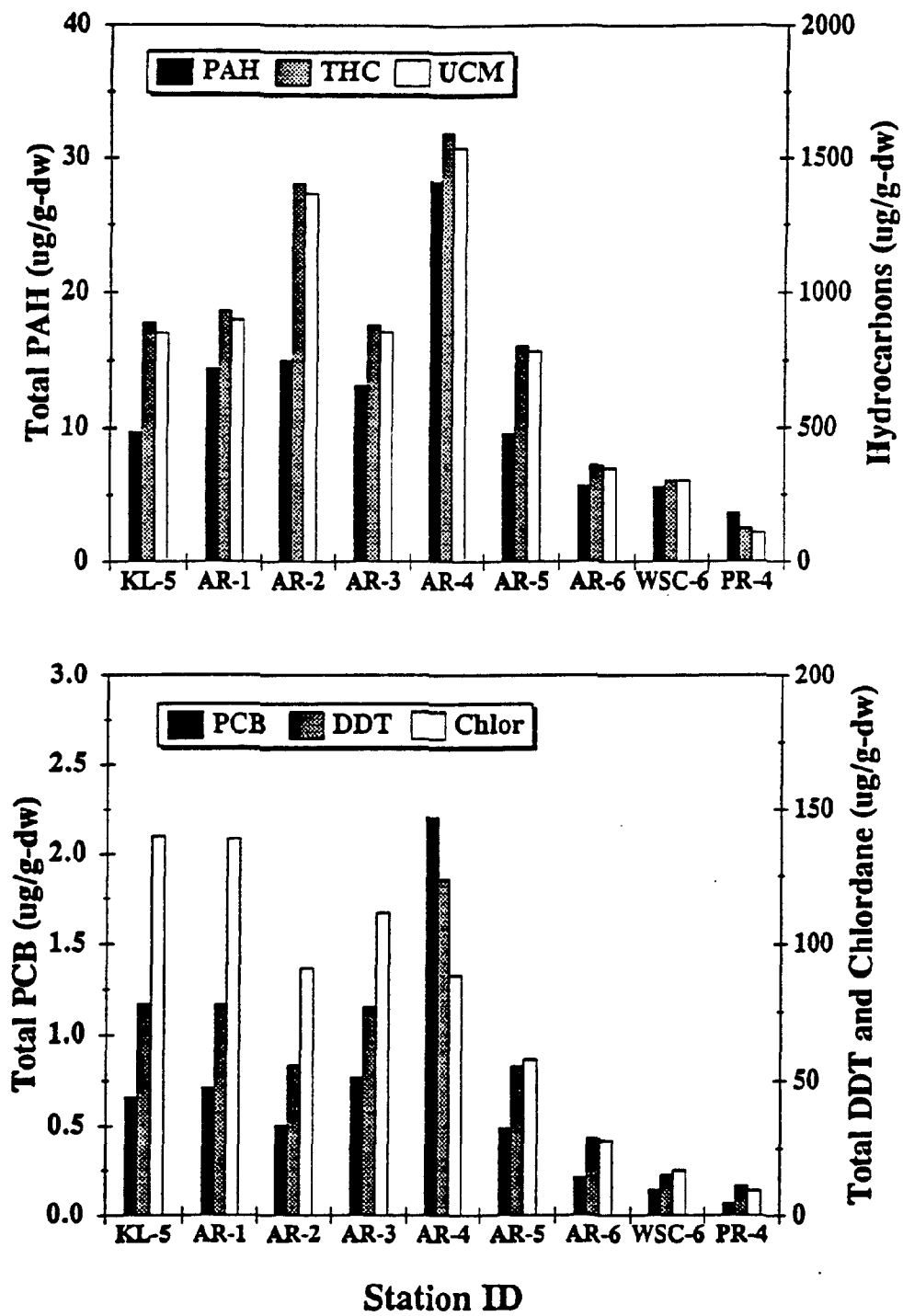
Figure 3. Outfall, sewer, and basin or channel sediment series of the Tidal Basin and Washington Ship Channel: Total PAH and Hydrocarbons.

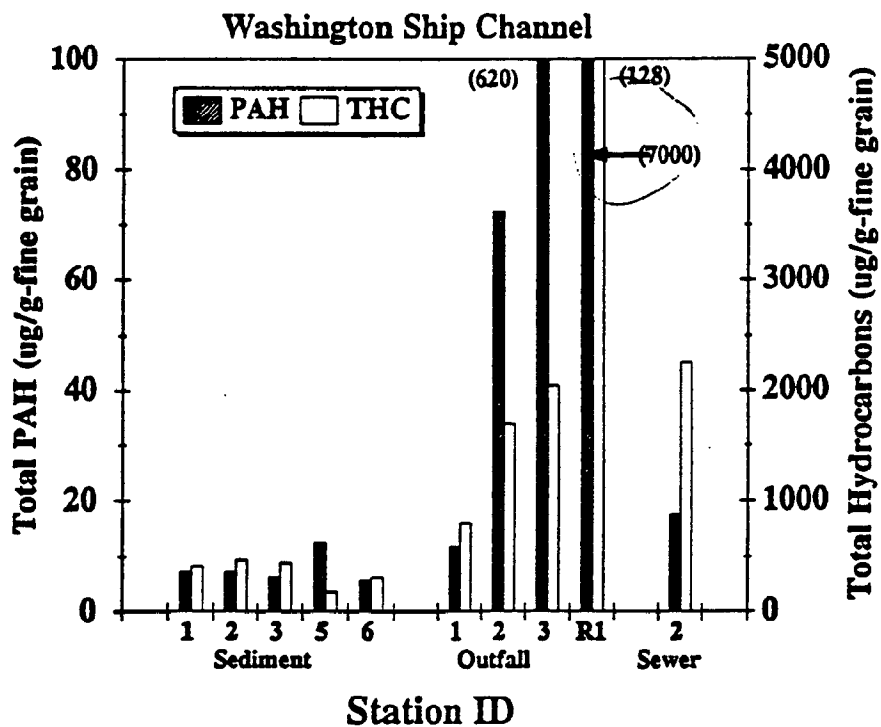
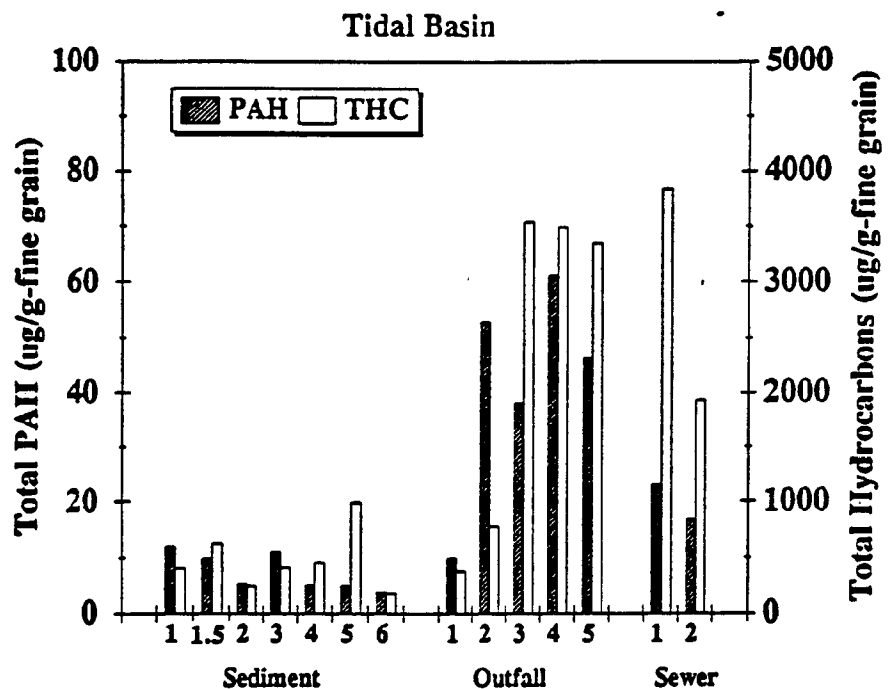
Figure 4. Outfall, sewer, and river sediment series in the Anacostia River: Total PAH and Hydrocarbons. The bottom panel highlights specific sewer and outfall series of the river.

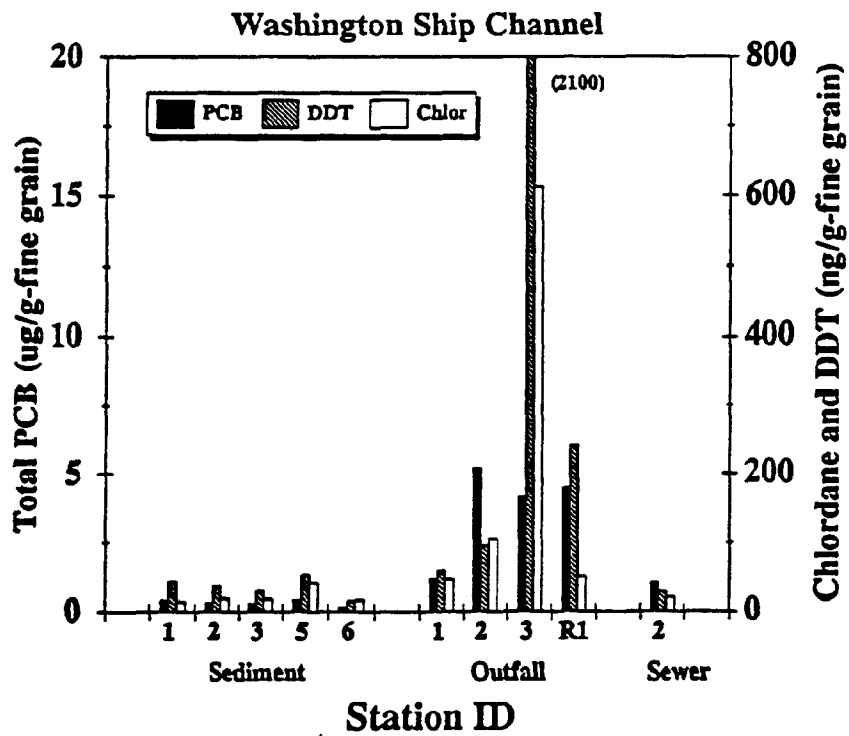
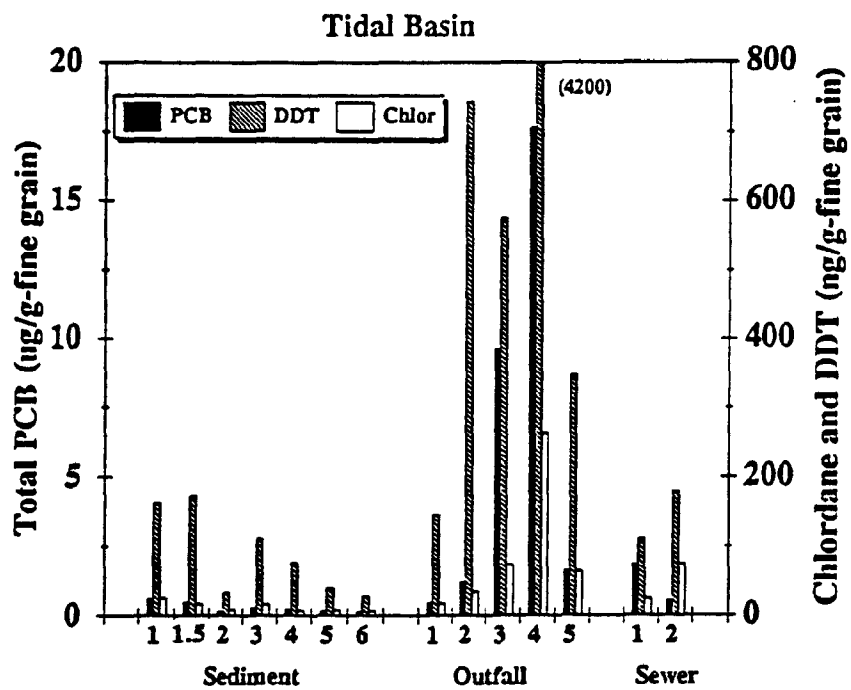
Figure 5. Outfall, sewer, and basin or channel sediments of the Tidal Basin and Washington Ship Channel: Total chlordanes, DDTs, and PCBs.

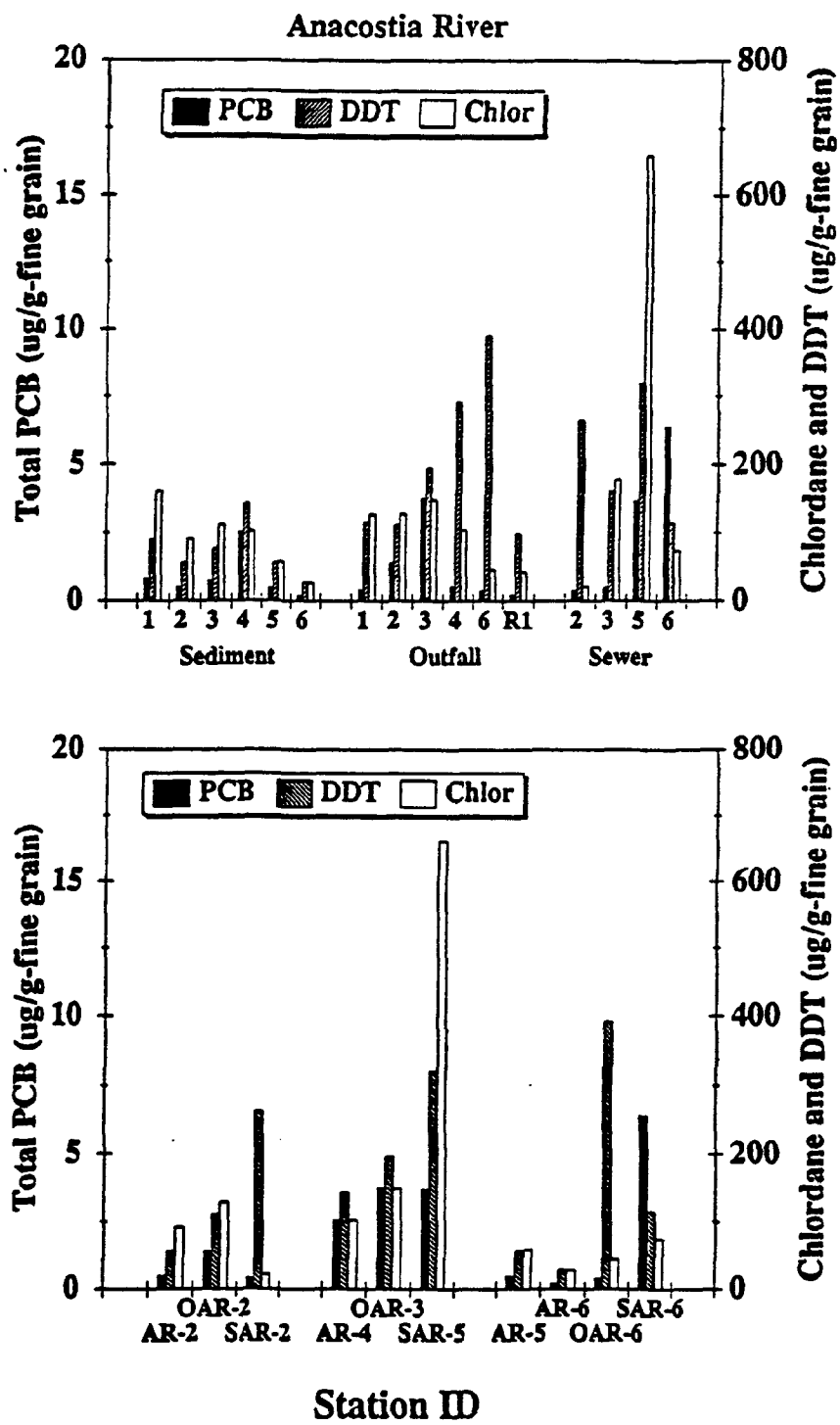
Figure 6. Outfall, sewer, and river sediments of the Anacostia River: Total chlordanes, DDTs and PCBs. The bottom panel highlights specific sewer and outfall series of the river.











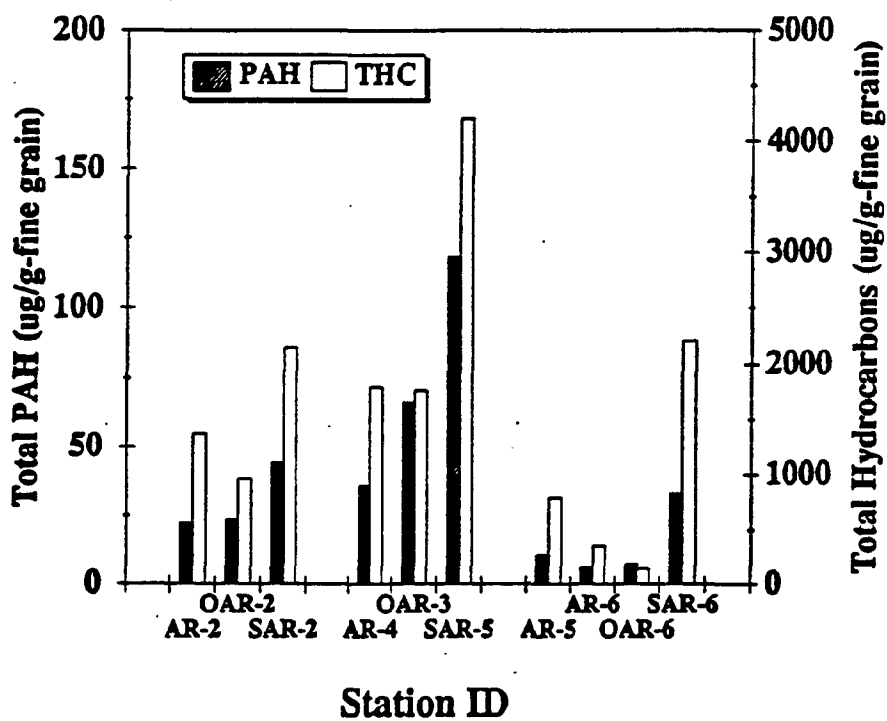
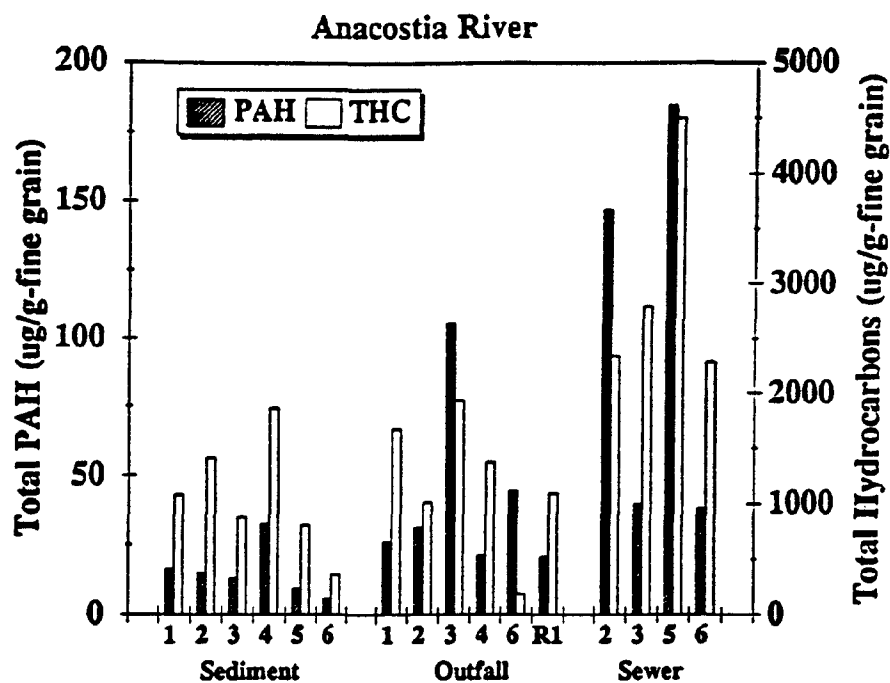


Fig 4 (Waste stat)

Reprint 4

**Distribution and Sources of Trace Metals
in Tidal River Sediments of Washington,
D.C.**

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Distribution and Sources of Trace Metals to Tidal River Sediments of Washington, D.C.

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Abstract

Fifty-four bottom sediments were collected from the Potomac and Anacostia rivers, Tidal Basin, and Washington Ship Channel in June 1991 to define the extent of trace metal contamination and elucidate source areas of sediment contaminants. Sediment samples also were collected directly in front of and within major storm and combined sewers that discharge directly to these areas. Trace metals (e.g., Cu, Cr, Cd, Hg, Pb and Zn) exhibited a wide range in values throughout the study area. Sediment concentrations of Pb ranged from 32.0 to 3630 $\mu\text{g Pb g}^{-1}$, Cd from 0.24 to 4.1 $\mu\text{g Cd g}^{-1}$, and Hg from 0.13 to 9.2 $\mu\text{g Hg g}^{-1}$, with generally higher concentrations in either outfall or sewer sediments compared to river bottom-sediments. In the Anacostia River, concentration differences among sewer, outfall, and river sediments, along with downriver spatial trends in trace metals suggest that numerous storm and combined sewers are major sources of trace metals. Similar results were observed in both the Tidal Basin and Washington Ship Channel. Cadmium and Pb concentrations are higher in specific sewers and outfalls, whereas the distribution of other metals suggest a more diffuse source to the rivers and basins of the area. Cadmium and Pb also exhibited the greatest enrichment throughout the study area with peak values located in the Anacostia River, near the Washington Navy Yard. Enrichment factors decrease in order of $\text{Cd} > \text{Pb} > \text{Zn} > \text{Hg} > \text{Cu} > \text{Cr}$. Between 70 and 96% of sediment-bound Pb and Cd were released from a N_2 -purged 1N HCl leach. On average, $\leq 40\%$ of total sedimentary Cu was liberated, possibly due to the partial attack of organic components of the sediment. Sediments of the tidal freshwater portion of the Potomac estuary reflect a moderate to highly contaminated area with substantial enrichments of sedimentary Pb, Cd and Zn. The sediment phase that contains these metals indicates the potential mobility of the sediment-bound metals if they are reworked during either storm events or dredging.

Introduction

Sediment contamination problems have been documented for an increasing number of marine and freshwater areas in the U.S. (Lyman et al. 1987; NAS 1989; NOAA 1990). Sediments are a major reservoir for anthropogenic contaminants (e.g., trace metals) due to the particle-reactive behavior and low water solubility of many pollutants (Young et al. 1985; Olsen et al. 1982). Trace metals in sediments can affect aquatic life as well as recreation and human health by entering the food chain (i.e., animal and plant life). Also, restrictions on the handling and disposal of contaminated sediments may raise the cost of dredging navigational waters to prohibitive levels. It is therefore imperative to have an accurate assessment of the extent of sediment contamination in a given location and knowledge of the source(s) of the pollutants.

There are few published data on the distribution and sources of potentially toxic inorganic and organic chemicals in the tidal freshwater rivers of the Washington, D.C. area. Studies by Pheiffer (1972) and Martin et al. (1981) indicated that the concentration of trace metals were highest around the District of Columbia and decreased downstream. Recent studies in the urban Potomac and Anacostia rivers have shown a wide range in organic and inorganic contaminant concentrations with limited areas of higher metal concentrations (ICPRB 1990).

Direct dumping, urban runoff, atmospheric deposition, and industrial and municipal discharges, as well as upstream runoff are some possible sources that contribute to the loadings of anthropogenic chemicals to riverine and coastal sediments. River runoff includes contributions from chemical weathering and erosional processes as well as upstream anthropogenic sources. While the extent of direct dumping is difficult to assess, Olsenholler (1991) estimated that urban runoff (e.g., street runoff) represents a major source of trace metals to the tidal Anacostia and Potomac rivers. In

older cities like the District of Columbia, a major source of trace metals and other contaminants is runoff from combined sewer outfalls (CSOs). Therefore, runoff and overflows through CSOs may have a substantial impact on the sediment quality in the Anacostia and Potomac rivers.

The spatial distribution of anthropogenic chemicals may help identify their source areas. Certain chemicals, for example, may have diffuse sources yielding distributions with no consistent geographical trend. Other chemicals, however, may have a specific source (i.e., point source) from either an industrial or municipal facility or chemical spill that would be indicated by higher sedimentary concentrations in a specific area. Different geographical trends may be reflected not just in concentration gradients but also by the distribution within certain groups of metals. The objectives of this study are to determine geographical trends, elucidate possible source areas, and discuss the sediment speciation of trace metals around the District of Columbia. To accomplish this, sedimentary concentrations of trace metals will be compared to concentrations in sediments sampled from sewers (both combined and storm) that drain into each respective area.

General Study Area

The District of Columbia (DC) lies along the fall line at the boundary between the Atlantic Coastal Plain and the Piedmont Plateau, and is at the head of navigation of the Potomac estuary (Fig. 1). The western and northern sections of the DC area are part of the Piedmont, which is underlain by deformed meta-sedimentary and meta-igneous rocks. From the mid-section of the city to the south is the Coastal Plain which contains unmetamorphosed fluvial and marine sediments (Reed and Obermeier 1989).

Presently, there are three major rivers or streams in the DC area: the Potomac and Anacostia rivers, and Rock Creek, which drains into the Potomac River just south of Georgetown (Fig. 1).

Average yearly flows for the Potomac River at Chain Bridge, Anacostia River, and Rock Creek are 1.03×10^{10} , 1.16×10^8 , and $5.5 \times 10^7 \text{ m}^3 \text{ yr}^{-1}$, respectively. Even though the drainage areas of the Anacostia River (310 km^2) and Rock Creek (160 km^2) are small compared to the Potomac River (e.g., at Chain Bridge, 29600 km^2), both water bodies drain predominantly urban environments.

During the past 200 years, the DC riverscape has been altered by sedimentation, dredging, and filling (Williams 1989). The Tidal Basin (surface area of 0.4 km^2), with an average depth of approximately 2 m, receives inputs from the Potomac River as well as storm water runoff and atmospheric deposition. The Washington Ship Channel, located in the southeastern section of DC, is connected to the Tidal Basin in the north section via a floodgate and to the Anacostia River at the southern end (Figure 1). The center of this channel has been dredged in the past with bottom depths ranging from $< 1 \text{ m}$ to approximately 8 m. The Washington Ship Channel is bordered by a park on the western side and residential/commercial development on the eastern side.

The flow of the Anacostia River is controlled by streamflow of the Northeast and Northwest branches, which join at Bladensburg (MD). The tidal waters in the lower Anacostia River, south of Bladensburg, have a long residence time (e.g., 35 days) due to the large volume relative to the runoff of the river. Therefore, it resembles a lake more than a river (Scatena 1987), and allows suspended sediments to settle within the tidal portion of the river. Sedimentation rates are reported to be $3.2 \text{ g cm}^{-2} \text{ yr}^{-1}$ or 1.9 cm yr^{-1} on a dry-sediment basis (Scatena 1987). While the center channel of the Anacostia River has been dredged in the past, depths outside the channel generally range from 0.5 to 5 m.

There is potential for historical contamination of the sediments in the study area due to past shipping and boating uses, and inputs via combined and storm sewer runoff. Approximately 30 storm and six combined sewers discharge into the lower Anacostia River (i.e., south of the Kingman Lake

area to Greenleaf Point at the mouth of the Washington Ship Channel). These sewers drain an area of approximately 14 km², or 22% of the drainage area of the Anacostia River within the District of Columbia. Approximately 54% of the total drainage area of the Anacostia Basin is urban (ICPRB 1988).

Numerous storm sewers (no combined) drain into the Tidal Basin and Washington Ship Channel. Of the six outfalls at the Tidal Basin, the largest drains the Constitution Ave. and Smithsonian Mall areas. The nine storm sewers that empty into the Washington Ship Channel drain an area from approximately Independence Avenue (Smithsonian Institution), 13th Street, and 4th Street, in southwest Washington, D.C. Numerous marinas also line the upper Washington Ship Channel.

Sampling and Analytical Methods

River and outfall sediment samples were obtained from the Tidal Basin (TB), Washington Ship Channel (WSC), Kingman Lake (KL), Potomac River (PR) and Anacostia River (AR) in June, 1991 (Fig. 1). In the Tidal Basin, six stations were sampled with six additional samples taken at the mouth of specific outfalls (OTB) that enter the basin. At one station (TB-5), three separate samples of three grabs each were taken within a radius of approximately 5 m to assess small scale spatial variability.

In the Potomac River, four stations were sampled from the mouth of Rock Creek to the confluence of the Anacostia and Potomac rivers and the Washington Ship Channel (Fig. 1). No samples were obtained from sewers that drain into the Potomac River. In the Washington Ship Channel, five stations were sampled along the eastern side of the channel. Seven stations were occupied in the Anacostia River. Anacostia River samples were taken on the northern side of the

river outside the main center channel. As in the Tidal Basin, one station from the Potomac and Anacostia rivers (PR-4 and AR-5, respectively) was sampled in triplicate (i.e., 3 separate samples of 3 grabs each).

Outfall and sewer sediment samples also were obtained from both the Anacostia River and Washington Ship Channel (Fig. 1). In the Washington Ship Channel, four outfall sediment samples (OWSC) were obtained in conjunction with one sample from a sewer (SWSC) that drains along Maine Ave., S.W. In the Anacostia River, six outfall sediment samples (OAR) were obtained as well as four (one combined and three storm) sewer samples (SAR) from various locations along the river. In Kingman Lake, a total of four sediment samples were obtained (Fig. 1), but no storm or combined sewer samples or outfall samples.

A Hydrolab Surveyor II was used to collect dissolved oxygen, temperature, conductivity, pH, and water depth just above the sediment surface. Sediments were collected with a stainless steel petite-Ponar grab sampler (0.023 m²) that was acetone rinsed at the beginning of each day. The sampler was inspected for possible cross-contamination (i.e., sediment from previous station) and rinsed with ambient water at each station. The top 2 to 3 centimeters of sediment not in contact with the sides of the sampler were removed and placed into a pre-cleaned Pyrex-glass bowl. This process was repeated three times until sufficient sediment was obtained.

Sediments were mixed with a pre-cleaned stainless steel spoon until homogeneous in both texture and color. Trace metal and grain size samples were placed into separate Zip-loc plastic bags. Sediment aliquots for acid-volatile sulfur (AVS) were sampled first and placed into 50 ml plastic centrifuge tubes and quickly frozen using dry ice (-78°C). All other samples were placed in coolers at approximately 4°C while in the field. Once on shore, sediment samples for metal and AVS analyses were placed in a freezer at -20°C, while samples for grain size were kept at 4°C.

All materials coming in contact with the samples were either glass or metal. All glass bowls were soaked in 0.5N HCl overnight, rinsed with distilled deionized water (DDW) and solvent rinsed with methanol, dichloromethane, then hexane (Burrick and Jackson, Inc.) and allowed to air dry in a hood. All metal utensils were washed similarly but without using the dilute acid rinse.

Sedimentary trace metals. Analyses for trace metals were identical to NOAA Status and Trends techniques (Brooks et al. 1988) and are briefly outlined. Samples were digested in 50 ml closed all-teflon "bombs" (Savillex Co.). Accurately weighed sediment aliquots (ca. 200 mg) were digested at 130°C in a mixture of nitric, perchloric and hydrofluoric acids. A saturated boric acid solution was then added to complete dissolution of the sediment and the digest was brought to a known volume. Standard reference materials and blanks were digested and analyzed with every batch of samples.

Concentrations of iron (Fe) and zinc (Zn) were determined by flame atomic absorption spectrometry (AAS), while sediment concentrations of cadmium (Cd), chromium (Cr), copper (Cu), and lead (Pb) were determined by a Perkin-Elmer Zeeman 3030, equipped with an HGA-600 furnace and AS-60 autosampler. Standard reference materials (e.g., NIST and NRCC) and spiked samples were used to evaluate analytical performance. Based on 10 separate analyses of the reference materials over the course of the project, the accuracy and precision of the analyses are approximately $\pm 10\%$ for all metals.

Mercury (Hg) was determined by cold vapor AAS on an aliquot of the same digest used to determine other trace elements following a "head space" sampling procedure (Brooks et al. 1988). A Laboratory Data Control Co. UV monitor with a 30 cm path length cell was used for Hg determinations.

Glassware, plasticware, and reaction vessels were cleaned first by soaking in Micro cleaning solution for 24 hrs and then rinsed with distilled water. Glassware and the reaction vessels were then

soaked in an acid bath (50%v/v HNO₃) for 24 hrs, rinsed with distilled deionized water (DDW), and air dried in a laminar flow hood in a dust free environment. Other plasticware used in these procedures were either used only a single time or reused after washing with Micro solution, appropriate acids (i.e., either HCl or HNO₃, depending upon resistance to attack) and DDW.

Acid Extractable Metals. Frozen sediment samples were quickly thawed and homogenized, with aliquots (ca. 1-2 grams) placed into pre-cleaned and tared 50 ml centrifuge tubes. Samples were accurately weighed and rapidly frozen using liquid nitrogen then stored at -20°C until extraction. Wet and dry weights were determined from separate aliquots of the sediment mix.

For extraction, samples were placed in a N₂-purged glove bag and allowed to thaw. De-aerated 1N HCl (Baker Intra-analyzed grade) was added to a volume of 25 ml and the centrifuge tubes were tightly capped. The samples were removed from the glove bag and mixed on a Vortex mixer for one hour. After centrifugation and filtration to separate the solids, samples were transferred to pre-cleaned screw cap polyethylene bottles and the metals analyzed by AAS.

While this leaching technique is not specific for a given sediment phase (Tessier et al. 1979), it should provide an indication as to the potential mobility (Forstner 1979) and possible biological availability of the trace metals (Luoma and Jenne 1976; Luoma 1983; Di Toro et al. 1990). Trace metals released under the conditions used in this study may derive from the exchangeable, carbonate, amorphous Fe/Mn oxides, and metal sulfide sediment phases along with a fraction of the organic component of the sediment (Tessier et al. 1979; Pickering 1981). Malo (1977) showed that a cold 0.3N HCl solution extracted a significant fraction of the metals from surface coatings and only minimal structural components are attacked. In this regard, a cold 1N HCl solution was shown to dissolve only natural and synthetic hydrous amorphous iron oxides, while leaving more crystalline oxides (e.g., magnetite, goethite, and hematite) intact (Chao and Zhou 1983). During this study,

sampling and extraction (i.e., in a N₂-purged glovebag), exposure of the sediments to air was kept to a minimum. Furthermore, field experiments showed no loss of acid-volatile sulfur (AVS) during sampling in the field (Velinsky unpublished data). Therefore, the contribution of metals that are bound or precipitated to the monosulfide phase should also be extracted using 1N HCl (Rapin et al. 1986).

To monitor precision and recovery of metals, several replicates of an in-house sediment standard (HS-2, collected from the Mississippi River Delta) were included in the preparation. Two unspiked replicates were analyzed, along with four replicates that were spiked with known amounts of analytes prior to sample processing. Two blanks were included to evaluate contamination which was insignificant compared to the concentrations observed.

Acid Volatile Sulfur. Acid volatile sulfur, predominantly iron sulfide, was determined by the method of Cutter and Oatts (1987). In brief, 20-80 mg of frozen sediment (wet/dry weight ratio determined on a separate aliquot) was extracted using 0.5N HCl and the evolved hydrogen sulfide (H₂S) was purged from the solution and trapped in a glass U-tube filled with Porapak QS, immersed in liquid nitrogen. After 15 min of purging and trapping, the U-tube was removed from the liquid nitrogen to volatilize the H₂S, which was chromatographically separated from other volatile compounds prior to detection by a photoionization detector. Detector signals were processed by a HP-3390A digital integrator/plotter.

Calibration of the detector was accomplished using a known quantity of anhydrous sodium sulfide (Alfa Products). Samples were run in either duplicate or triplicates and precision was generally better than 10% as relative standard deviation.

Organic Carbon and Grains Size. Total organic carbon (OC) was determined by infra-red absorption after combustion in an O₂ stream, using a LECO WR-12 Total Carbon System. Sediment grain size

was determined by the procedure of Folk (1974), utilizing sieving to separate gravel and sand fractions from the clay and silt fractions. The latter fractions were subsequently separated by the pipette (settling rate) method. Detailed descriptions of the methods utilized in measuring OC, CaCO_3 , and grain size are reported in Brooks et al. (1988).

Results

Sediment Organic Carbon and Grain Size

Organic carbon (OC) concentrations ranged between 2.5 and 6.4% on a dry-weight basis (dw) for all river and basin sediment samples with an average of $4.0 \pm 0.9\%$ OC (\pm standard deviation; Table 1). Highest concentrations were observed in Kingman Lake and the Tidal Basin. Outfall sediment samples exhibited a greater range in OC concentrations than bottom sediments, with concentrations ranging from 0.7 to 11% OC. This wide range most likely reflects both the different possible sources of OC and the physical sorting of particles (both size and composition) during runoff events.

The grain size distribution in the study area was fairly uniform, with river sediments predominately in the clay and silt size fractions ($< 63 \mu\text{m}$; Table 1). At a few stations, the sand fraction accounted for between 25 and 30% (e.g., WSC-5, PR-1 and TB-3) of the total sediment. These locations may be areas of stronger currents in which fine-grain sediments do not settle. Outfall and sewer sediment samples exhibited a greater range in grain size, reflecting the physical sorting of particles in these often high-flow environments (Table 1).

Sewer sediment samples exhibited lower concentrations of OC than either river or outfall sediments, with concentrations averaging $1.0 \pm 0.9\%$ OC ($n=5$) for both storm and combined sewer sediments. The lower concentrations of OC also were reflected in the grain size distribution of these samples in which approximately 80% of the samples were in the sand-sized fraction. However, there

was no significant relationship ($p > 0.01$, $n=50$) between %OC and the fraction of fine-grain sediment for the entire data set.

Distribution and Geographic Trends of Sedimentary Trace Metals

The distribution of individual trace metals, presented on a whole-sediment basis (i.e., weight of metal per weight of dry whole-sediment), exhibited similar geographic trends within each river or basin (Table 2). In the Potomac River, highest trace metal concentrations were found at station PR-1 (Table 2). Downstream from this station, sedimentary concentrations of all trace metals decreased, with station PR-4 exhibiting some of the lowest concentrations throughout this study. While no samples were taken upstream of Rock Creek as part of this study, previous studies (Pheiffer 1972; ICPRB 1991) revealed lower concentrations in the upstream area (i.e., from Little Falls to Georgetown).

Concentrations of trace metals in Tidal Basin sediments were similar at all sites except for Cu and Pb at station TB-1 (Table 2). Sediment concentrations of Cu and Pb at TB-1 were 120 and 204 $\mu\text{g g}^{-1}$ compared to 56.1 ± 8.0 and $93.8 \pm 12.8 \mu\text{g g}^{-1}$ (average of five stations) in the basin, respectively. Grain size variations were small and do not account for the differences between TB-1 and the other stations (Table 1).

Within the Washington Ship Channel, the distribution of all sedimentary trace metals reveal highest values at the head of the channel (i.e., stations WSC-1, 2, and 3) with decreasing concentrations downstream (Table 2). Lead concentrations decreased from elevated values of 183 and 125 $\mu\text{g Pb g}^{-1}$ at WSC-1 and WSC-3, respectively, to a low of 48.3 $\mu\text{g Pb g}^{-1}$ at WSC-5. At station WSC-6, located at the confluence of the Washington Ship Channel and the Anacostia River, all trace metals increased in concentration from those at WSC-5.

Results from the Anacostia River are presented as a transect from KL-5, located outside

Kingman Lake in the river, to PR-4, located just south of Hains Point at the confluence of the Potomac and Anacostia rivers (Fig. 1). This transect includes WSC-6, located at the confluence of the Anacostia River and the Washington Ship Channel. From station KL-5 to AR-3 (just upstream of the Washington Navy Yard), concentrations of Hg, Pb, Zn, and Cd were fairly constant, while concentrations of Cr and Cu increased slightly (Table 2; Fig. 2). Sediment concentrations of all trace metals were highest at station AR-4. The increase in trace metal concentrations from KL-5 and AR-3 to AR-4 was greatest for Hg, Pb and Cd with increases of 206%, 179% and 60%, respectively. Sedimentary concentrations of all trace metals decreased downstream of AR-4. The largest decreases were exhibited by Hg, Pb and Cd; concentrations decreased 600%, 1000% and 450%, respectively, from AR-4 to PR-4. The general decrease in trace metal concentrations was not related to grain size, as 90% of the sediment from stations between AR-5 and PR-4 was composed of silt and clay.

Triplicate sediment sample analyses revealed little variability in the distribution of all trace metals in the "local" area (i.e., within a 5 m radius). Relative standard deviations (\pm SD/mean \times 100; $n = 3$) for all metals, TOC, and grain size were below 10%. Due to modest variations in grain size, these results suggest that local-scale spatial variations in concentrations are small compared with larger geographical changes observed in the Potomac and Anacostia rivers, and the Tidal Basin. This may not be the case where sediment grain size and other bulk characteristics vary substantially.

Comparison between Sediments, Outfalls, and Sewers

For comparison of sedimentary trace metal concentrations between river, outfall and sewer sediment samples, concentrations were divided by the fraction of fine-grain sediment in each sample (i.e., sediment particles $\leq 63\mu\text{m}$). This normalization procedure assumes that no contaminants are associated with the sand-sized material, which only dilutes the level of contamination for a given sample (NOAA 1991). Due to grain size differences between river, outfall, and sewer samples,

normalization of the data resulted only in small changes of river or basin sediment trace metal concentrations, but significant concentrations increases from the outfall and sewer samples.

Samples collected at five storm sewer outfalls draining the Tidal Basin area had elevated trace metal concentrations compared with basin sediments (Fig. 3). Material collected at OTB-4 and OTB-3 had the highest trace metal concentrations of the study (Fig. 3), with concentrations of Pb and Hg at station OTB-4 of 1.9% Pb (i.e., $19400 \mu\text{g Pb g}^{-1}$ fine-grain) and $50 \mu\text{g Hg g}^{-1}$ fine-grain, respectively. As a comparison, sedimentary concentrations in the Tidal Basin ranged from 80 to $210 \mu\text{g Pb g}^{-1}$ fine-grain and 0.3 to $0.5 \mu\text{g Hg g}^{-1}$ fine-grain, respectively. Elevated concentrations of Cu, Cd, and Zn also were evident at stations OTB-4 and OTB-3, compared with Tidal Basin sediments (Fig. 3). Two sediment samples (STB-2) collected from a sanitary sewer that drains the area along 15th Street, S.W., had extremely elevated concentrations of most metals (Table 2). Concentrations of Pb and Cd ranged from 1 to 8% Pb (fine-grain) and 5.5 to $24 \mu\text{g Cd g}^{-1}$ fine-grain, respectively. This location was sampled twice during the study and concentrations of most metals exhibited substantial variation (Fig. 3).

Trace metal concentrations of outfall sediment samples surpassed those in the sediments of the Washington Ship Channel (Fig. 4). Concentrations of most trace metals increased from station OWSC-1 to OWSC-3 then decreased slightly at OWSC-R1. For example, Pb concentrations ranged from 190 to $2400 \mu\text{g Pb g}^{-1}$ fine-grain between OWSC-1 and OWSC-3, respectively, with highest concentrations at station OWSC-3. One storm sewer was sampled in the Washington Ship Channel area (SWSC-2). This sewer drains a small area between 9th and 10th Streets on Maine Avenue in southwest Washington D.C.. The runoff from this area eventually feeds a larger storm sewer line that flows into the Washington Ship Channel near it's head. Sewer-sediment trace metal concentrations were greater than the channel sediments, but not as high as some of the outfall

concentrations (Fig. 4). However, the concentration of Cd ($17 \mu\text{g Cd g}^{-1}$ fine-grain) in this sewer sediment sample was substantially higher than samples from the outfall or channel (overall range = 0.7 to $5.4 \mu\text{g Cd g}^{-1}$ fine-grain).

As with the other sites, sediment concentrations of most trace metals decreased from sewer and outfall samples to the river sediments within the Anacostia River (Fig. 5). This is most evident between the storm sewer SAR-5 and its outfall OAR-3, and the river station AR-4. Station SAR-5 is located "up-pipe" from the outfall OAR-3 which is slightly upstream from station AR-4. Within this series, the concentration of Pb decreased from $970 \mu\text{g Pb g}^{-1}$ fine-grain at SAR-5 to $780 \mu\text{g Pb g}^{-1}$ fine-grain at OAR-3. The concentration of sedimentary Pb decreased further to $480 \mu\text{g Pb g}^{-1}$ fine-grain at AR-4. Sediment collected at station OAR-3 could be a mixture of outfall material and river sediments, reflecting the lower concentrations found in the river. Similar trends at these stations are noted for the trace metals Hg, Cd, and Zn (Fig. 5).

Dilute Acid-Leachable Metals

To obtain a better understanding of the sediment phase(s) that controls the distribution and cycling of trace metals, 15 river and basin sediment samples were extracted with a 1N HCl solution under a N_2 -purged atmosphere.

A substantial fraction of sediment-bound Cd and Pb and to a lesser extent Zn and Cu, were released from the acid leach (Table 3). For all sediments, between approximately 70 and 96% of the total Cd and Pb was extracted, with an average of $84 \pm 8\%$ Cd and $83 \pm 11\%$ Pb ($n=15$), while overall only $63 \pm 8\%$ of the total sedimentary Zn was present in the 1N HCl fraction. On average, $\leq 40\%$ of the total sedimentary Cu was liberated, possibly due to the partial attack of the organic component of the sediment. Copper has been shown to be strongly complexed or bound to organic matter, and the 1N HCl solution may only partially release the Cu bound to this fraction. Oxidizing

acids or hydrogen peroxide would be better suited to release trace metals bound in the organic fraction (Tessier et al. 1979; Martin et al. 1987). Only $25 \pm 4\%$ of the total sedimentary Fe was released by this technique indicating that a significant fraction of the Fe is either more crystalline oxides, pyrite, or lattice bound. The Fe liberated from the sediments is most likely a combination of both amorphous iron oxides and iron monosulfide phases (i.e., FeS).

Discussion

Information on the sources and geochemistry of trace metal contamination are critical to management of the problem in the District of Columbia as well as other urban tidal freshwater environments. In the following sections, these topics are discussed to help determine the fate of contaminated sediments in urbanized estuaries.

Sources of trace metals in the Washington, D.C., area

The geographical distributions observed in this study indicate that sources located within the Washington, D.C., area are major contributors to the levels of trace metals found in the sediments. Land and street runoff through the area's storm and combined sewer system are major sources. Also, drainage from streams flowing through the District of Columbia also can account for elevated levels of metals in various sections of the Potomac and Anacostia rivers. In this regard, runoff from Rock Creek to the Potomac River is the likely source of metals concentrations of the sediments around the confluence (Fig.1). Studies by Phieffer (1972) and ICPRB (1990) in the area upstream of the confluence revealed lower or similar concentrations of metals compared to downstream of Rock Creek. The drainage area of Rock Creek is approximately 60% urban, with numerous storm water discharges into the creek. These discharges are most likely the source of the higher concentrations found at the confluence.

The Tidal Basin sediments are most likely influenced by storm water sewers that empty into it

(Fig. 1). The elevated concentrations observed at OTB-3 and 4 suggest that runoff through these pipes is a major source of metals to the basin. These sewers drain the street area around 15th and D Street, and near Interstate 395, in southwest Washington, D.C. Because these pipes are storm sewers, runoff from the numerous streets and highways in this area are a probable source. However, the elevated concentrations of metals, especially Pb, in the sanitary sewer line adjacent to the basin indicates an additional source. Prior to approximately 1990, the Bureau of Engraving and Printing (BEP) discharged approximately 5 kg Pb day⁻¹ to the sanitary system. While this material was sent to the Blue Plains Wastewater Treatment Plant (WWTP) for treatment and disposal, overflows into the storm sewer system have been reported. (Friebele 1991). These overflows could be a possible source of Pb to the Tidal Basin and other waterbodies within the District of Columbia. In 1990, a pretreatment facility was completed to collect Pb and other contaminants before discharge to Blue Plains WWTP. Although it is impossible to estimate the flux of trace metals to the basin from this data set, the concentration gradients suggest that material flowing through these outfalls (i.e., samples were taken directly in front of an outfall in the basin) are a dominant source of trace metal contamination to the basin. Once the contaminants are introduced into the basin, dispersal of the fine-grain material and associated trace metals yield the observed concentrations measured in the basin.

The upper end of the Washington Ship Channel is a semi-enclosed embayment in which the water is partially flushed once per tidal cycle from water stored in the Tidal Basin. Numerous bridges, both automotive and railroad, cross the upper end of the waterbody as well as four storm sewers that drain into the upper end of the channel. As in the Tidal Basin, the concentration differences between outfall and channel sediments, indicate that runoff from storm sewers is a major source of trace metals. The higher concentrations of sedimentary trace metals at stations WSC-1, WSC-2, and WSC-3 (Fig. 4) correspond to the higher concentrations at the outfall stations OWSC-

R1, OWSC-3, and to a lesser extent OWSC-2. Station OWSC-3 is near a storm sewer that drains the area between 12th and 13th Streets, S.W. (Fig. 4). This area was the site of a railroad yard and is the site of numerous construction projects.

Trace metals distributions in the Anacostia River suggests a substantial source between stations AR-3 and AR-4 and that runoff through OAR-3, is a source of trace metal contamination to this section of the Anacostia River. The concentration differences between sewer, outfall and river sediment samples at SAR-2, OAR-2 and AR-2 also indicate a source of trace metals from the sewer system (Fig. 5). Concentrations of Pb and Zn at SAR-2, for example, are 37000 and 2300 $\mu\text{g g}^{-1}$ fine-grain, respectively. Concentrations decreased at OAR-2, the outfall of the combined sewer from which SAR-2 was taken. This decrease is most likely related to the mixing of river sediments with outfall material. Station AR-2 is located slightly upstream of the outfall, and has concentrations lower than, or similar to, the outfall sediments.

The gradual increase in sediment concentration of Cr, Cu, and Zn from KL-5 to AR-4 suggests a more diffuse input for these metals. Runoff from the numerous combined and storm sewers that empty into this area, along with upstream transport are possible sources. Also, the river width increases in this segment of the Anacostia as it approaches the Potomac River. This increase, along with the tides, may extend the residence time of the water, enabling particulate material and associated-metals to settle to the bottom and incorporate into the sediments (Scatena 1987).

Trace metal concentration gradients between sewer, outfall, and river sediment samples suggest that runoff from the stormwater and combined sewer system is a major source of contaminants to the Anacostia River, Washington Ship Channel and Tidal Basin (Figs. 3, 4, and 5). In all areas, highest sediment concentrations of trace metals were measured from either the sewer or outfall sediments. Concentrations of Pb, Hg, and Cd, for example, were as high as 37000, 50, and

24 $\mu\text{g g}^{-1}$ fine-grain, respectively, in either the outfall or sewer samples. The trends in concentration between sewer, outfall and river sediments are especially noted at station AR-4 in the Anacostia River. While this data set indicates that runoff through the sewer system is a major source of trace metals to the area, the magnitude of this source compared to other sources (e.g., atmospheric deposition, direct runoff, dumping) can not be quantified directly. Also, due to the nature and types of samples taken it impossible to pinpoint a specific source of trace metals. However, these results indicate specific areas of concern that warrant further investigation.

Dilute acid-leachable metals

Results indicate that the mobility of trace metals in these sediments may be substantial. As a result of dredging or storm events, the redox environment of the surface sediment can change, liberating weakly-associated trace metals. These changes can be the result of oxidation of reducing sediment, and possible pH changes in weakly-buffered pore waters of freshwater sediments. These metals could then be potentially more available for biological uptake and transport via water. For example, sediments in the rivers or basin contained a substantial amount of acid-volatile sulfur (AVS) which only exists in reducing conditions (Table 1; Goldhaber and Kaplan 1975). This sulfide fraction in these sediments is most likely metal monosulfides (e.g., XS, where X can be Fe, Cd, Cu, Pb, and Zn). Aeration of the sediment could release metals into the pore waters until they are bound into other phases such as Fe/Mn oxides (Lion et al. 1982). The oxidation of AVS (and pyrite) also could lower the pH of the sediments enhancing the release of metals to the pore waters. These results indicate that a substantial fraction of sedimentary metals could be released during events that rework or transport the sediments (i.e., bioturbation, storm events, and dredging).

Excess metals in the sediments around Washington, D.C.

A useful tool in expressing the degree to which a sediment is impacted from anthropogenic

sources of trace metals is the enrichment factor (EF) (Trefrey and Presely 1976; Sinex and Helz 1981; Helz et al. 1985; Windom et al. 1989). Normalization of the sediment to a reference element not associated with anthropogenic influences is a convenient approach to determine the degree of sediment contamination. Elements such as aluminum (Al) (Windom et al. 1989; Schropp et al. 1990), lithium (Li) (Loring 1990) and iron (Fe) (Trefrey and Presely 1976; Sinex and Helz 1981; Helz et al. 1985) have been used in the past. For this study, Fe was chosen as a normalizing element because 1) it is the fourth most abundant metal in the earth with a crustal average of 3.5% (Wedepohl 1971); 2) in most cases, anthropogenic sources are small compared to the amount of Fe naturally present; and 3) the ratio of metal to Fe is fairly constant in the Earth's crust. The enrichment factor is defined as: $EF = (X/Fe)_{\text{sediment}} / (X/Fe)_{\text{unimpacted sediment}}$, where X/Fe is the ratio of the trace metal (X) to the amount of Fe in the sample.

In using the EF, a comparison to a sediment that is unimpacted by anthropogenic sources is necessary [i.e., $(X/Fe)_{\text{unimpacted}}$]. Critical in this analysis is the choice of metal to Fe ratio for "unimpacted" sediments. Past studies have compared sediments to the distribution of trace metals in the earth's crust (Sinex and Helz 1981; Helz et al. 1985). While this approach is useful, it may not account for natural variations in sediment types of different geological regions. One way to account for this variability is to derive a ratio from "unimpacted" sediments in the general area of interest (Windom et al. 1989; Schropp et al. 1990). In the present study, all samples have the potential to be impacted above natural levels. Therefore, data from samples taken in the Chesapeake Bay drainage area (including the Potomac River) were used to derive metal abundances in the general area (NOAA 1991). Sixteen stations in Chesapeake Bay that are relatively remote from such anthropogenic sources as Baltimore Harbor and Elizabeth River were used. The ratios obtained from the regression of the NOAA (1991) data are presented in Table 4 along with data from other areas. The ratios derived

from Helz et al. (1985) are from the average composition of coastal plain deposits from northern Chesapeake Bay, while the data from core 1314 (Goldberg et al. 1978) are from a location just south of the mouth of the Potomac River. These data, along with values from average continental crust and soils, are similar in magnitude (Table 4). Therefore, the average values were used to calculate the EF for each metal.

The degree to which sediments in the study area are enriched in trace metals vary from metal to metal. These variations can be due to a number of factors including 1) choice of $(X/Fe)_{unimpacted}$, 2) biogeochemistry of the metal, and 3) sources of metals to the study area. While these calculations use the average $(X/Fe)_{unimpacted}$, these values can vary. For example, the Cd/Fe value ranges from 0.01 to 0.09 while the Pb/Fe value ranges from 4.0 to 9.4. While these values may change the magnitude of the EF, the geographic trends should not change. In light of these factors some general trends and features are obtained from the EF data (Table 5).

The EFs are generally highest for Cd and lowest for Cr and Hg (Table 5), with intermediate values for Pb and Zn. Except for Hg, all trace metals are enriched in Kingman Lake and the upper Anacostia River (KL-1 to AR-4). This is especially evident at station AR-4, which has the highest EF in the study area for all trace metals. The EF decreases in order of $Cd > Pb > Zn > Hg > Cu > Cr$ at station AR-4. Other stations also indicate higher enrichments (and possible sources) of trace metals. These include WSC-1, 2, and 3 in the upper end of the Washington Ship Channel; station PR-1 at the mouth of Rock Creek in the Potomac River; and TB-1 in the northern embayment of the Tidal Basin. The order of enrichment (i.e., $Cd > Pb > Zn > Hg > Cu > Cr$) for these stations are similar to AR-4 with some small variations between Hg and Cu.

The EFs indicate potential anthropogenic sources for trace metals in the sediments of the Washington, D.C., area. These source materials are enriched in Cd and Pb relative to the other

metals (Table 5). Areas that are impacted more by anthropogenic sources include the mouth of Rock Creek, the northern embayment of the Tidal Basin, the upper end of the Washington Ship Channel, and the upper Anacostia River and Kingman Lake. The enrichment in the Tidal Basin is likely due to the large storm sewer that drains the area around the Mall of the Smithsonian and Constitution Ave. In the Anacostia River, increased levels of enrichment at AR-4, just downstream of the Washington Navy Yard, are probably due to the storm and combined sewers located just above this station. The degree to which stations above AR-4 are enriched may be due to multiple sources and a net deposition of sediment in this area. From KL-1 to AR-4 there are numerous storm and combined sewers that drain into this area, while in the Kingman Lake area (KL-1 to KI-4), runoff from RFK Stadium and the surrounding environment could be a major source of trace metals.

One of the goals of this study was to describe the extent and degree of contamination in this area. Enrichment factors provide a geochemical basis for this description, while a more-subjective description is obtained by comparing these data to concentrations in other areas. In this regard, the selection of studies can bias the interpretation of the degree of contamination between locations. For this reason, only data from the Chesapeake Bay and Delaware Bay will be utilized.

The ranges presented in Table 6, for the present study are for river and basin sediments only. Sewer and outfall sediment samples are not included. Sediment concentrations of Cd, Cu, Hg, and Pb in this study are higher than those found in the mainstem Chesapeake Bay by a factor of 2 to 4, dependent on the metal (Table 6). Concentrations of all metals are well below those found in Baltimore Harbor and the Schuylkill River (Delaware River basin). Compared with the estuarine portion of the Potomac River (i.e., MDE stations MLE2.2, XDA11, and XEA659; MDE, unpublished data), sediment concentrations of all metals are higher in the Washington, D.C. area, reflecting its proximity to the urban runoff source.

Summary and Conclusions

The geographic and spatial trends for trace metals in sediments reveal specific areas of concern within the Washington, D.C. area. These locations are indicated by increased sediment concentrations of trace metals relative to adjacent locations within the study area. In many cases, most trace metals exhibited the same spatial concentration gradient with elevated concentrations observed in many areas, such as near the Washington Navy Yard (AR-4), at the confluence of Rock Creek and the Potomac River (PR-1), and in the upper Washington Ship Channel (WSC-1 to WSC-3). Furthermore, concentration gradients between sewer, outfall, and river sediment samples strongly suggest urban runoff as the major source of these contaminants. This is especially noted at station AR-4 located just downstream of the Washington Navy Yard, near the South Capitol Street Bridge. While the extreme gradient between the sewer, outfall, and river sediments at this location indicates urban runoff as a source, past and present activities at the Washington Navy Yard could also contribute to the contamination of the area. The net result of all these possible sources are substantially higher concentrations of all contaminants at AR-4. The large concentration decrease downstream from this area suggests a possible higher source function at AR-4 and/or a greater retention of upstream sources (i.e., fine-grain sediments) in this section of the river.

The sediment of the urban Potomac and Anacostia rivers reflect a moderate to highly contaminated location with substantial enrichments of sedimentary Pb, Cd, Zn, and possible Hg. The source of these metals is most likely urban runoff, however upstream sources and atmospheric deposition can not be ruled out. The sediment phase or phases that contain these metals indicate a potential mobility of these sediment-bound metals if the sediments are disturbed during, for example, storm events and dredging.

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Table 1. Bulk sediment characteristics for the various study areas^a.

Sta. ID.	TOC (%)	SAND (%)	SILT (%)	Clay (%)	AVS ($\mu\text{mol S g}^{-1}\text{-dw}$)
<u>Kingman Lake</u>					
KL-1	4.05	12.8	50.3	36.9	12.9
KL-2	4.02	3.0	68.8	28.3	11.8
KL-3	4.06	0.20	67.1	32.7	12.7
KL-4	4.95	12.9	54.3	32.8	9.2
KL-5	6.08	11.1	54.6	34.3	4.8
<u>Anacostia River</u>					
KL-5	6.08	11.1	54.6	34.3	10.8
AR-1	3.89	13.9	53.4	32.7	7.5
AR-2	3.99	0.54	63.2	36.2	7.5
AR-3	2.98	0.53	70.9	28.6	26.4
AR-4	4.30	14.0	59.2	26.9	17.0
AR-5A	3.75	0.69	71.4	27.9	ND
AR-6	3.57	0.86	67.7	31.4	ND
OAR-1	4.89	9.7	61.6	28.7	ND
OAR-2	3.44	9.0	68.2	22.8	ND
OAR-3	2.62	77.7	20.2	2.2	ND
OAR-4	4.68	10.7	61.3	28.0	ND
OAR-6	6.08	16.8	52.9	30.3	ND
OAR-R1	0.66	44.9	33.9	21.2	ND

Sta. ID.	TOC (%)	SAND (%)	SILT (%)	Clay (%)	AVS ($\mu\text{mol S g}^{-1}\text{-dw}$)
SAR-2	1.02	78.2	21.4	0.48	ND
SAR-3	0.28	85.6	14.2	0.15	ND
SAR-5	2.50	78.6	19.9	1.5	ND
SAR-6	0.84	77.4	20.9	1.7	ND
<u>Washington Ship Channel</u>					
WSC-1	3.21	1.5	72.2	26.3	83.0
WSC-2	2.89	0.42	80.2	19.4	ND
WSC-3	3.37	0.33	84.2	15.4	47.6
WSC-5	2.54	31.5	50.7	17.8	ND
WSC-6	3.74	0.71	69.8	29.5	ND
OWSC-1	3.30	15.1	72.9	12.0	ND
OWSC-2	11.1	38.5	51.5	10.0	ND
OWSC-3	2.87	78.6	20.4	1.1	ND
OWSC-R1	8.76	39.3	23.3	37.4	ND
SWSC-2	0.37	75.5	24.0	0.55	ND
<u>Potomac River</u>					
PR-1	3.86	21.9	45.8	32.3	ND
PR-2	2.41	13.2	51.8	35.1	ND
PR-3	3.92	9.6	55.0	35.4	ND
PR-4A	4.14	5.8	59.9	34.3	4.2

Sta. ID.	TOC (%)	SAND (%)	SILT (%)	Clay (%)	AVS ($\mu\text{mol S g}^{-1}\text{-dw}$)
<u>Tidal Basin</u>					
TB-1	6.37	2.9	69.9	27.2	1.0
TB-1.5	4.13	1.3	73.6	25.1	ND
TB-2	3.02	0.68	35.1	35.1	ND
TB-3	4.70	21.3	46.6	32.1	20.4
TB-4	3.30	0.45	76.5	23.1	ND
TB-5a	3.10	1.2	67.7	31.1	ND
TB-6	3.37	0.63	73.5	25.9	ND
OTB-1-1	ND	ND	ND	ND	ND
OTB-1-2	3.00	19.4	71.4	9.1	ND
OTB-2	1.98	80.1	18.6	1.4	ND
OTB-3	1.89	86.6	12.5	0.94	ND
OTB-4	1.88	81.3	16.5	2.2	ND
OTB-5	2.34	77.4	21.0	1.6	ND
STB-2-1	9.69	60.7	33.5	5.8	ND
STB-2-2	11.0	48.6	47.8	3.6	ND

*Station IDs. starting with the prefix (O) indicate samples that were taken directly in front of a sewer outfall, while ID's starting with the prefix (S) indicates samples that were taken in a sewer. Stations AR-5, PR-4 and TB-5 were sampled and analyzed in triplicate and the average value is reported. AVS is acid-volatile sulfur. ND - Not Determined.

Table 2. Concentrations of trace metals in the sediments of the various study areas^a.

Sta. ID.	Cd	Cr	Cu	Fe	Hg	Pb	Zn
<u>Kingman Lake</u>							
KL-1	1.53	106	63.8	4.07	0.28	134	348
KL-2	2.21	134	92.3	5.04	0.43	184	466
KL-3	2.19	118	100	4.73	0.39	177	450
KL-4	1.92	106	96.6	4.19	0.46	199	462
KL-5	2.01	107	76.1	4.38	0.35	144	418
<u>Anacostia River</u>							
AR-1	1.72	103	75.6	3.91	0.34	139	355
AR-2	1.93	118	91.9	4.56	0.29	148	401
AR-3	1.96	124	102	4.82	0.37	157	406
AR-4	3.18	156	127	4.19	1.04	409	512
AR-5A	1.48	108	90.2	5.23	0.36	131	367
AR-6	0.92	90.3	63.8	4.82	0.54	83.2	279
OAR-1	1.72	11	73.4	4.01	0.30	164	420
OAR-2	1.75	116	145	4.25	1.21	185	450
OAR-3	0.90	58.0	69.9	1.54	0.72	175	215
OAR-4	1.43	109	86.9	4.08	0.30	151	382
OAR-6	0.50	74.0	94.7	3.73	1.16	111	208

Sta. ID.	Cd	Cr	Cu	Fe	Hg	Pb	Zn
OAR-R1	0.29	31.0	19.9	1.79	0.17	40.0	80.0
SAR-2	0.79	634	328	3.63	0.18	8140	512
SAR-3	0.37	163	20.5	2.38	0.01	102	224
SAR-5	1.68	133	97.4	1.64	2.02	207	271
SAR-6	0.45	122	47.9	1.43	0.22	96.0	164
<u>Washington Ship Channel</u>							
WSC-1	1.19	94.3	103	5.06	0.74	183	356
WSC-2	1.03	95.5	99.9	4.99	0.58	147	332
WSC-3	1.09	90.7	92.6	5.24	0.52	126	339
WSC-5	0.45	51.1	33.4	2.92	0.23	48.3	137
WSC-6	0.79	86.8	52.6	4.76	0.25	61.9	247
OWSC-1	1.25	83.0	102	3.33	0.64	163	400
OWSC-2	3.31	105	251	3.56	0.63	425	1090
OWSC-3	0.95	63.0	112	1.51	0.20	515	406
OWSC-R1	3.05	167	348	4.11	0.87	2100	750
SWSC-2	4.07	44.0	27.6	1.16	0.05	72.0	200
<u>Potomac River</u>							
PR-1	0.99	96.2	59.7	4.45	0.56	128	365
PR-2	0.55	66.6	34.2	3.89	0.15	32.0	168
PR-3	0.52	63.4	35.6	3.76	0.13	33.9	171
PR-4A	0.58	69.0	37.8	4.06	0.15	39.0	188

Sta. ID.	Cd	Cr	Cu	Fe	Hg	Pb	Zn
<u>Tidal Basin</u>							
TB-1	1.67	97.4	120	4.89	0.45	204	385
TB-1.5	ND	ND	ND	ND	ND	ND	ND
TB-2	0.84	91.1	55.1	4.55	0.25	84.5	255
TB-3	0.74	75.9	44.5	3.89	0.24	109	216
TB-4	0.97	96.9	66.7	5.09	0.29	104	292
TB-5A	0.83	87.0	55.3	4.67	0.27	79.3	260
TB-6	0.93	92.3	59.1	4.88	0.27	91.4	285
OTB-1-1	0.24	41.0	19.7	0.89	0.07	36.0	62.0
OTB-1-2	0.83	30.0	47.9	1.67	0.15	120	235
OTB-2	0.43	28.0	13.7	1.91	0.06	320	112
OTB-3	0.89	167	25.9	2.50	0.09	1020	180
OTB-4	0.94	176	102	2.89	9.22	3630	527
OTB-5	0.73	149	39.4	2.32	0.13	465	197
STB-2-1	9.46	3060	1780	7.07	7.03	31300	1240
STB-2-2	2.81	518	510	1.89	4.96	5020	684

*All concentrations are in μg per gram dry-weight, except for Fe which is %. Station IDs. starting with the prefix (O) indicate samples that were taken directly in front of a sewer outfall, while ID's starting with the prefix (S) indicates samples that were taken in a sewer. Stations AR-5, PR-4 and TB-5 were sampled and analyzed in triplicate, these data are the average. ND - Not Determined.

Table 3. Ratio of Acid Extractable to Total Sedimentary Metals from Selected Stations^a.

Sta. ID.	Cd	Cu	Fe	Pb	Zn
KL-1	0.94	0.35	0.21	0.80	0.69
KL-2	0.91	0.47	0.27	0.98	0.72
KL-3	0.89	0.47	0.24	0.80	0.57
KL-4	0.91	0.38	0.24	0.78	0.72
KL-5	0.79	0.55	0.21	0.79	0.52
AR-1	0.88	0.39	0.26	0.91	0.74
AR-2	0.92	0.51	0.24	0.93	0.73
AR-3	0.92	0.56	0.25	0.94	0.73
AR-4	0.74	0.13	0.27	0.85	0.67
AR-5	0.87	0.48	0.24	0.84	0.60
WSC-1	0.92	0.40	0.33	0.96	0.62
WSC-3	0.77	0.34	0.37	0.88	0.58
PR-4A	0.77	0.43	0.19	0.67	0.50
TB-1	0.70	0.43	0.24	0.70	0.53
TB-3	0.72	0.23	0.25	0.59	0.60
Average	0.84	0.41	0.25	0.83	0.63
± SD	0.08	0.11	0.04	0.11	0.08

^aKL-Kingman Lake, AR-Anacostia River, WSC-Washington Ship Channel,

PR-Potomac River, TB-Tidal Basin.

Table 4. Metal to Iron Ratios used for the Calculation of Enrichment Factors (EF)^a.

Cd	Cr	Cu	Hg	Pb	Zn	Location
0.03	20.0	8.5	0.01	4.2	17.0	Continental Crust ^b
ND	18.8	9.2	ND	9.4	25.0	Soils ^c
0.01	11.8	3.6	ND	4.4	14.1	St. Mary's County Coastal Deposit ^d
0.01	24.0	2.1	ND	3.9	14.5	Ann Arundal County Deposits ^e
0.09	9.4	8.1	0.06	NS	NS	Chesapeake Bay Sediments ^f
0.05	23.0	8.1	ND	NS	NS	Core 1314 ^g , Mouth of Potomac River
0.04	17.8	6.6	0.04	5.5	17.7	Average
0.03	6.0	3.0		2.6	5.1	± Standard Deviation (1σ)

^aValues are the ratio of total metal ($\mu\text{g g}^{-1}$) to total Fe (%). ^bWedepohl 1971; ^cMartin and Meybeck 1979; ^dHelz et al. 1985; ^eNOAA 1991; ^fGoldberg et al. 1978. ND - No Data; NS - regression between metal and iron was not significant at $p < 0.05$, whereas other metals were significant at $p < 0.01$ ($n = 50$).

Table 5. Trace metal enrichment factors (EF) for the sediments of the Washington, D.C. area^a.

Sta. ID.	Cd	Cr	Cu	Hg	Pb	Zn
<u>Kingman Lake</u>						
KL-1	9.4	1.5	2.4	1.7	6.0	4.8
KL-2	11.0	1.5	2.8	2.1	6.7	5.2
KL-3	11.6	1.4	3.2	2.1	6.8	5.3
KL-4	11.5	1.4	3.5	2.7	8.7	6.2
KL-5	11.5	1.4	2.6	2.0	6.0	5.4
<u>Anacostia River</u>						
AR-1	11.0	1.5	2.9	2.2	6.5	5.1
AR-2	10.6	1.4	3.1	1.6	5.9	4.9
AR-3	10.2	1.4	3.2	1.9	5.9	4.8
AR-4	19.0	2.1	4.6	6.2	17.7	6.9
AR-5A	7.1	1.2	2.6	1.7	4.5	4.0
AR-6	4.8	1.1	2.0	2.8	3.1	3.3
<u>Washington Ship Channel</u>						
WSC-1	5.9	1.0	3.1	3.7	6.6	4.0
WSC-2	5.2	1.1	3.0	2.9	5.3	3.8
WSC-3	5.2	1.0	2.7	2.5	4.4	3.7
WSC-5	3.9	1.0	1.7	1.9	3.0	2.7
WSC-6	4.1	1.0	1.7	1.3	2.4	2.9

Sta. ID.	Cd	Cr	Cu	Hg	Pb	Zn
<u>Potomac River</u>						
PR-1	5.6	1.2	2.0	3.2	5.2	4.6
PR-2	3.5	1.0	1.3	1.0	1.5	2.4
PR-3	3.5	0.9	1.4	0.9	1.6	2.6
PR-4A	3.6	1.0	1.4	0.9	1.8	2.6
<u>Tidal Basin</u>						
TB-1	8.5	1.1	3.7	2.3	7.6	4.5
TB-1.5	ND	ND	ND	ND	ND	ND
TB-2	4.6	1.1	1.8	1.4	3.4	3.2
TB-3	4.8	1.1	1.7	1.6	5.1	3.1
TB-4	4.8	1.1	2.0	1.4	3.7	3.2
TB-5A	4.5	1.0	1.8	1.4	3.1	3.1
TB-6	4.8	1.1	1.8	1.4	3.4	3.3

*Enrichment factor = $(X/Fe)_{\text{sediment}} / (X/Fe)_{\text{unimpacted}}$, where X is the trace metal of interest and the $(X/Fe)_{\text{unimpacted}}$ values are taken from Table 4. ND - No data.

Table 6. Ranges of trace metal from various studies in the Mid-Atlantic region^a.

Cd	Cr	Cu	Hg	Pb	Zn	Location	Source
0.45 - 3.2	51 - 133	33 - 126	0.2 - 1.0	32 - 409	137 - 512	Washington, D.C.	This Study ^b
<1 - 650	60 - 5750	60 - 2930	0.1 - 10	130 - 13890	350 - 6040	Baltimore Harbor	Lyman et al. (1987)
ND ^c	10 - 880	10 - 3000	<0.01 - 0.9	20 - 19000	30 - 1400	Schuykill River, PA.	Lyman et al. (1987)
0.2 - 1.3	39 - 62	29 - 43	0.07 - 0.3	15 - 73	134 - 270	Potomac Estuary	MDE ^d (unpub. data)
0.09 - 0.60	90 - 237	15 - 30	0.1 - 0.2	11 - 23	42 - 86	Lower Ches. Bay	NOAA (1991)
0.09 - 0.40	77 - 647	20 - 75	0.1 - 0.4	8.5 - 27	57 - 115	Middle Ches. Bay	NOAA (1991)
0.25 - 0.96	108 - 280	56 - 79	0.2 - 0.5	18 - 80	93 - 380	Upper Ches. Bay	NOAA (1991)

^aConcentrations are in µg per gram dry-weight. ^bOnly river or basin sediment samples are presented for this study. ^cND - No data. ^dMDE - Maryland

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Figure 1. General study area showing the locations of the Tidal Basin, Washington Ship Channel, Kingman Lake and the Potomac and Anacostia rivers. Arrows located around the shoreline indicate approximate location of outfall and sewer samples.

Figure 2. Sediment trace metal distribution: Anacostia River. Transect is from the southern portion of Kingman Lake (KL-5) to the confluence of the Anacostia and Potomac rivers and the Washington Ship Channel at station PR-4.

Figure 3. Distribution of selected trace metals in outfall, sewer, and basin sediments of the Tidal Basin. Concentrations of Pb are in %.

Figure 4. Distribution of selected trace metals in outfall, sewer, and channel sediments of the Washington Ship Channel.

Figure 5. Distribution of selected trace metals in outfall, sewer, and river sediments of the Anacostia River. Concentrations of Pb are in %.

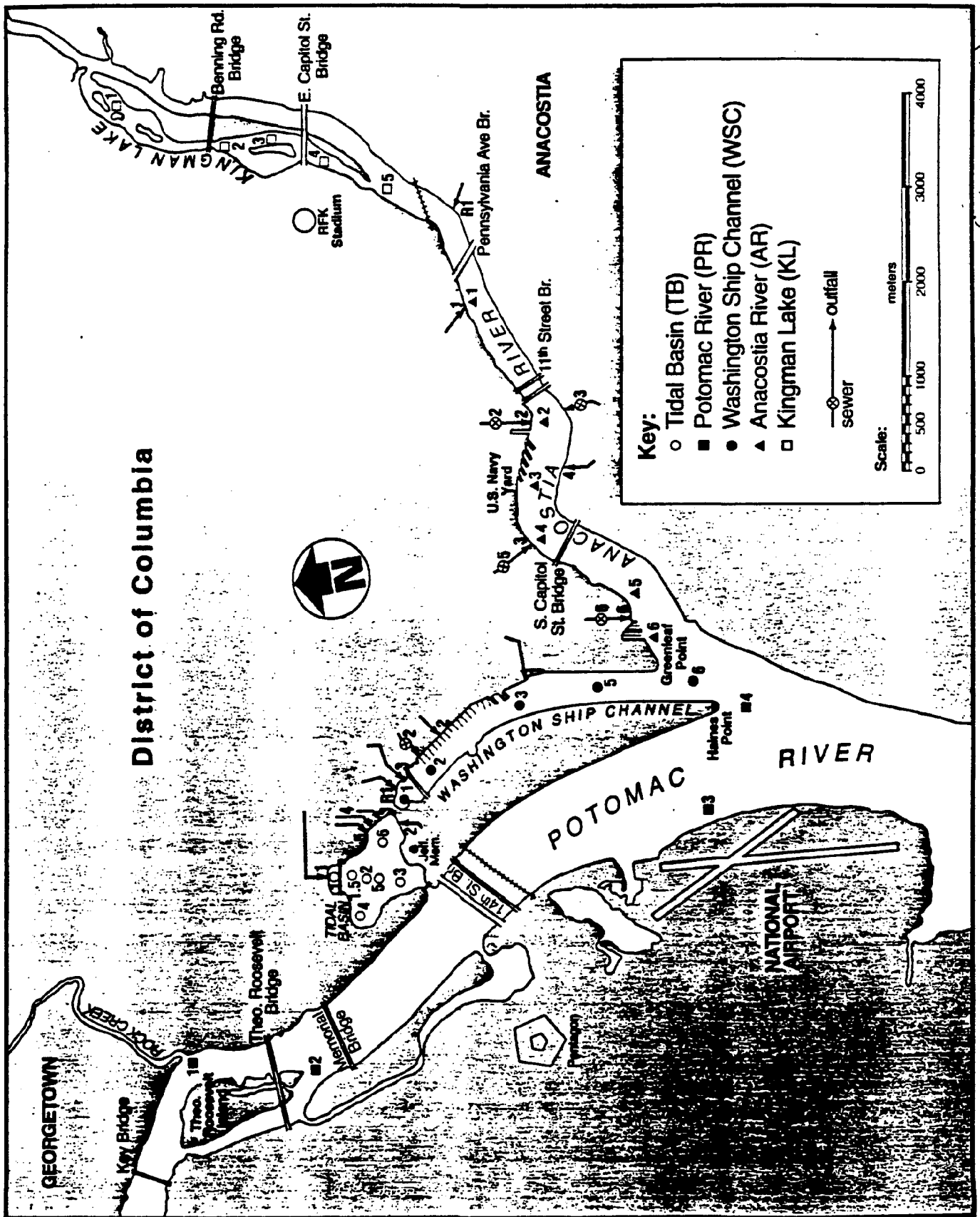
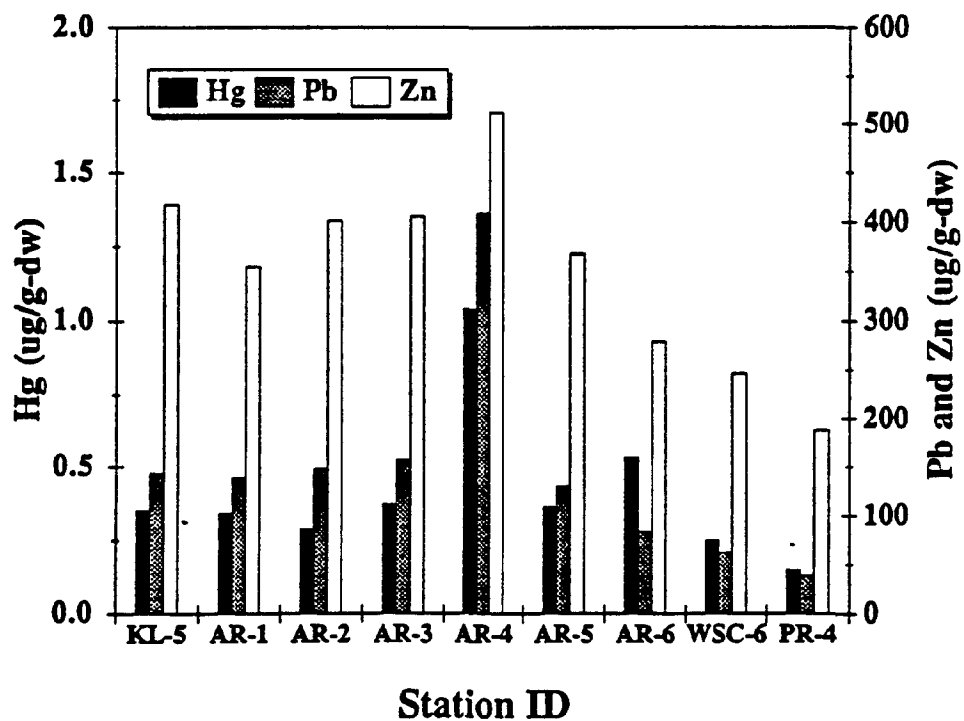
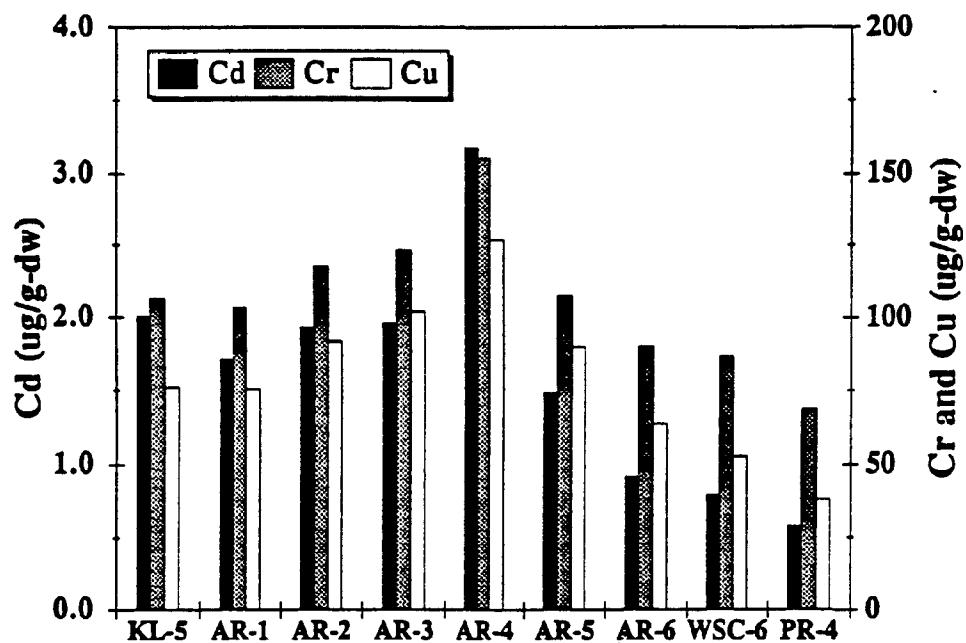
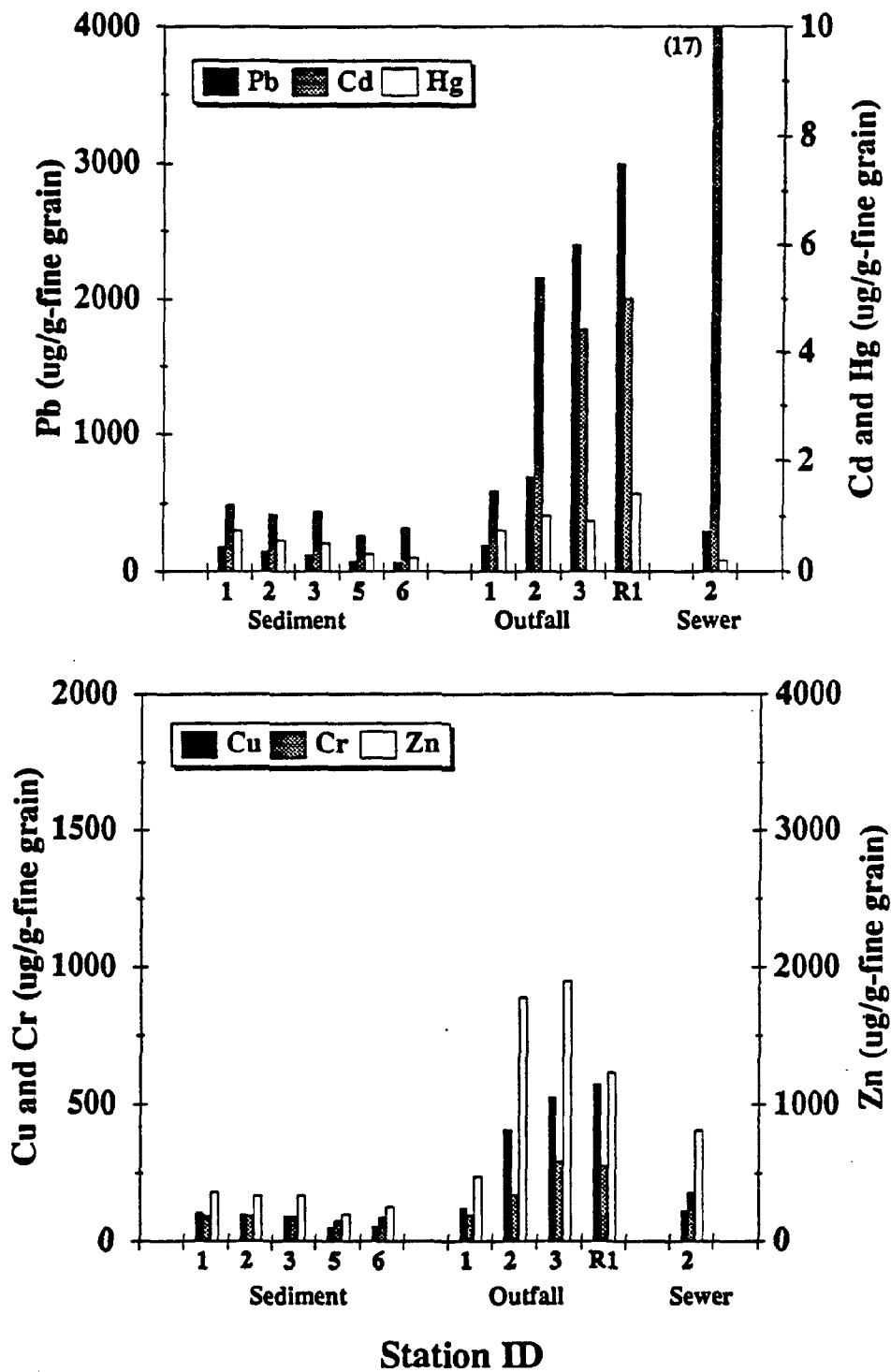
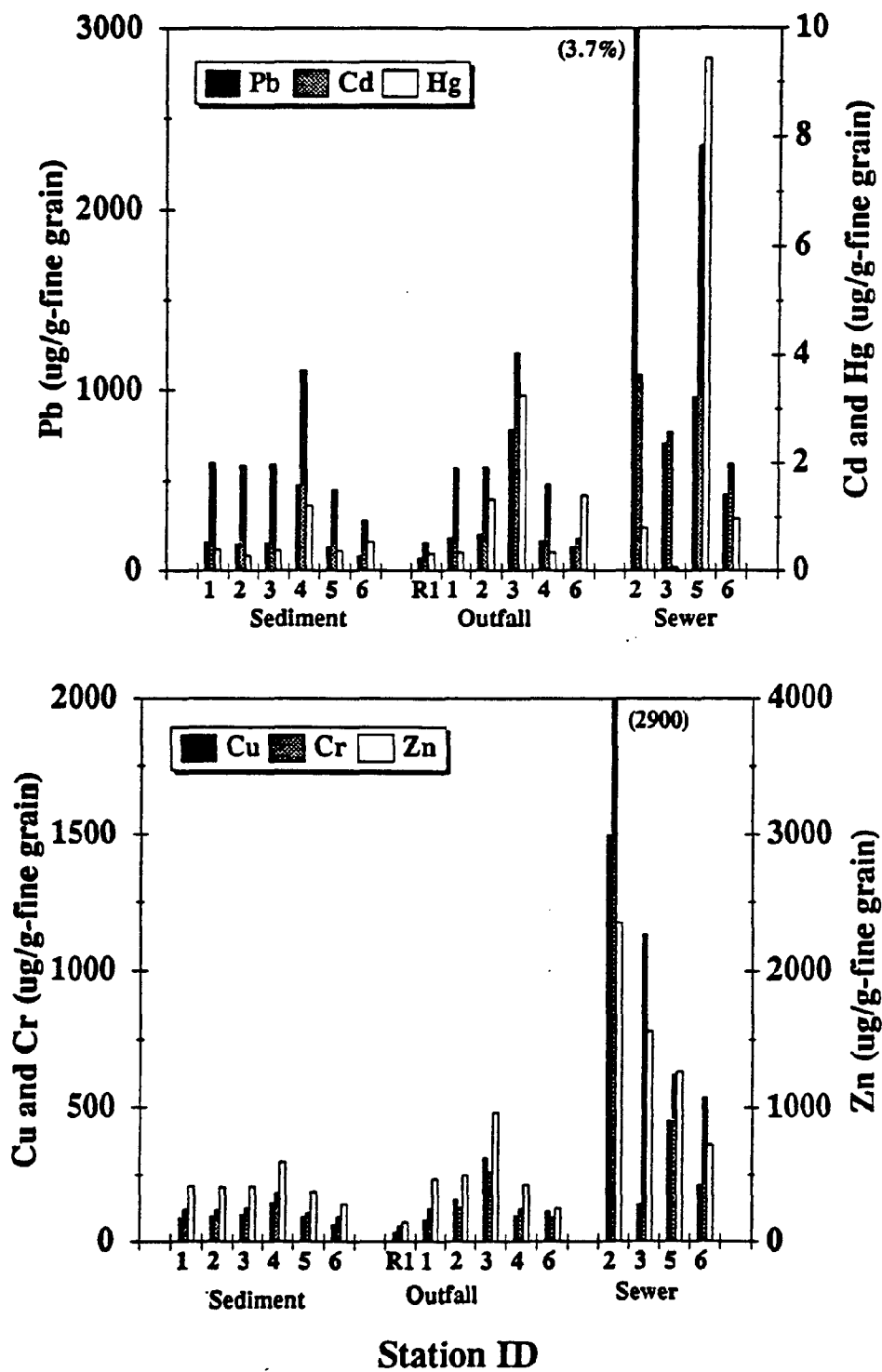
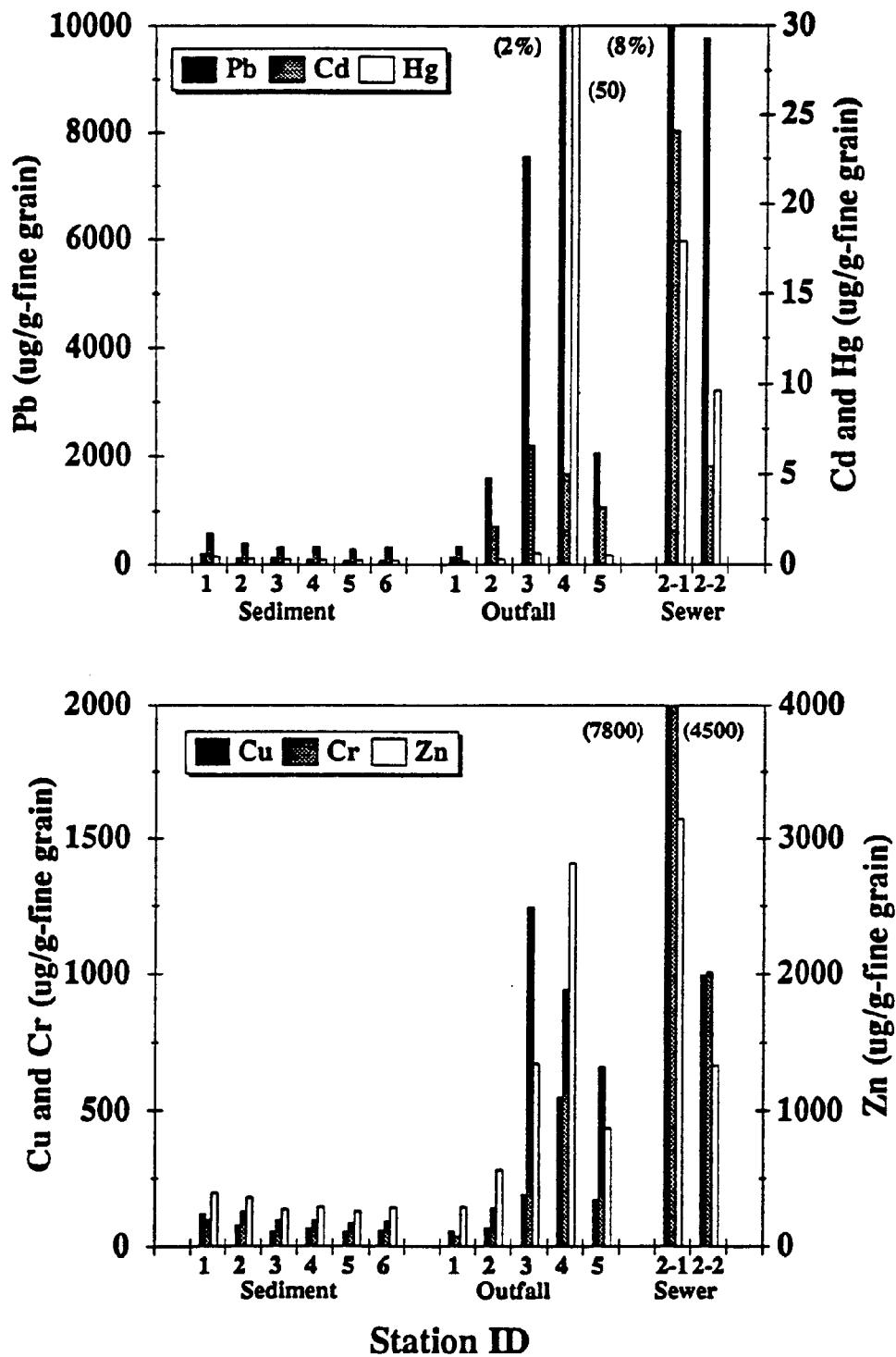


Fig. 1. (Velinsky et al.)









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